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‘Natural biosorbents for the removal of metals from aqueous solutions’

by

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ABSTRACT

The removal of metals from potable and wastewater to regulatory standards presents unique challenges. Conventional treatments, chemical precipitation, adsorption by activated carbon, ion-exchange, electro-chemical and reverse osmosis can be expensive or ineffective at low concentrations. Recent research has shown that biosorption by low cost biomass can be an effective alternative. Biosorption is the passive (non-metabolic) uptake and concentration of metals by non-viable biological materials.

In this work, natural materials and shellfish processing wastes were physio-chemically characterised to identify products with suitable characteristics to perform as biosorbents. Brown seaweed (*Fucus vesiculosus*), Douglas fir wood bark (*Pseudotsuga menziesii*), peat and carapace from the edible crab (*Cancer pagurus*) were assessed for Cu(II) removal as a function of time and concentration. Mechanically and commercially milled carapace (MMC and CMC) were the most efficient, removing >95.0 % within 40 minutes from 100-1000 mg/L Cu(II) solutions. Extended studies showed MMC was also applicable for use in biosorption columns and effective for the removal of Cd(II), Hg(II), Pb(II), Ni(II) and Zn(II), at concentrations ranging from 1-1000 mg/L.

MMC and CMC were compared with chitin, chitosan, Darco® and Norit® activated carbons and Dowex® ion-exchange resin for the removal of Cu(II). Dowex® and Norit® were the most efficient commercial sorbents removing up to 99.9 % from the 1-1000 mg/L. MMC and CMC compared favourably and were effective over the 1-4000 mg/L range and suitable for use in acidic solutions (pH 4.2-4.7).

Sorption of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC were predicted reliably (R²>0.99) using a pseudo-second-order model, with rates of 1.34, 14.6, 1.37 and 1.30 mg/mg/min respectively. An intra-particle diffusion model and SEM-EDAX micro-analysis revealed that the biosorption of metals proceeds via rapid adsorption-precipitation to surface binding sites, followed by rate limiting intra-particle diffusion. Equilibrium uptakes were evaluated using the Langmuir, Freundlich and Redlich-Peterson adsorption isotherm models. The best fits were obtained for the Langmuir model with 416.7, 86.2, 30.5 and 14.6 mg/g MMC for Pb(II), Cu(II), Zn(II) and Hg(II) respectively.

The results show that biosorption of metals is complex and proceeds via adsorption, precipitation, absorption, and ion exchange depending on pH, initial concentration and material conditioning. Although CMC was marginally more efficient than MMC, MMC is less labour intensive and more cost effective to produce. Therefore, MMC offers significant potential as a viable metal biosorbent and merits further development.
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1. CHAPTER 1 INTRODUCTION LITERATURE REVIEW
1.1. INTRODUCTION

“We never know the worth of water till the well is dry” Thomas Fuller, (1732). Water is a precious natural resource and essential for the life of everything on Earth, (Food and Agricultural Organisation (FAO) Water Resources Development, 2007). Current estimates vary from source to source, but approximately 1.2 billion people have no access to safe drinking water and 2.6 billion suffer from inadequate sanitation through lack of water, (United Nations World Water Development Report, 2006). With growing demands on national and global water reserves, increasing population and more widespread pollution, the provision of high-quality drinking water and treatment of wastewaters will present unique challenges over the next century (Breach, 1997; Ferrier and Edwards, 2002; World Water Day, 2007).

A specific concern is the presence of dissolved metals such as aluminium, copper, chromium, zinc, cadmium, lead and mercury. These metals are potential toxins and can be bio-accumulated and magnified through food webs, causing serious health and environmental concerns, even at dilute concentrations (Chang et al., 1998). Source reduction and the implementation of effective waste management programmes are the preferred long term solutions to reduce metal emissions to the environment. However, upgrading existing treatment systems and the introduction of new and novel technologies will continue to play a vital role (UN Water Development Report, 2006).

The following sections aim to highlight some of the health and environmental issues associated with metal pollution in aquatic environments, provide an overview of the current treatment processes for the removal of metals and introduce some of the emerging biological processes.
1.2. METALS IN THE AQUATIC ENVIRONMENT

Surface water often contains suspended solids (Bencala, 1984; Islam et al., 2004), gases (EA Report SCO30155/SR2, 2005), minerals (Le Roux, 2005), organics (Hope et al., 1993) and metals that exceed regulatory limits (Guisti et al., 1993). Unlike organics, metals don’t biodegrade but persist in the environment indefinitely (Florence et al., 1992 and Guinee et al., 1999). Consequently, dissolved and complexed metals can pose health and environmental threats depending on their toxicity and bioavailability (Clearwater et al., 2002; Franklin et al., 2002; Leonard et al., 2004).

1.2.1 Metal sources

Metals are released to the environment by physical and chemical weathering processes and the biochemical actions of plants and soil biota (Langdon et al., 2003; Gadd, 2004). While some metals are naturally abundant (e.g. aluminium and iron), others are rare (e.g. mercury and cadmium) with low background concentrations (Elder, 1988). The amount of metals released into natural waters is dependant on the geological characteristics, type of soil and the flora and fauna found in the watersheds (Foster and Charlesworth, 1996). Other natural sources include volcanic emissions (Pyle and Mather, 2003) and changing environmental conditions (Nelson and Campbell, 1991; Tipping et al., 2003; Blake et al., 2003; Macdonald and Fyfe, 2005).

Anthropogenic activities, such as the application of agrochemicals (Edwards et al., 1990 and Nicholson et al., 2003), industrial discharges (Gaballah et al., 1994; Gupta et al., 2000; Pavlish et al., 2003) can increase metal concentrations above natural background levels. Mining and construction activities can also increase toxic metal concentrations in soils and aqueous systems (Zoumis et al., 2000 and Loredo et al., 2006). Table 1.1 shows the metal concentration ranges found in aqueous environments can vary considerably.
Table 1.1: Concentration ranges of selected metals found in aquatic environments

<table>
<thead>
<tr>
<th>Water body</th>
<th>Al</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oceans (ng/L)</td>
<td>0.50-2.09</td>
<td>1.50-4.0</td>
<td>0.01-0.05</td>
<td>0.25-0.3</td>
<td>0.50-1.0</td>
<td>0.003-0.3</td>
<td>0.003-0.30</td>
<td>0.5-1.7</td>
<td>0.10-2.0</td>
</tr>
<tr>
<td>Freshwater (µg/L)</td>
<td>100-1000</td>
<td>1000-1000</td>
<td>0.5-0.6</td>
<td>0.27-0.34</td>
<td>0.31-0.38</td>
<td>0.01-0.1</td>
<td>0.58-0.96</td>
<td>0.1-1.0</td>
<td>0.43-0.78</td>
</tr>
<tr>
<td>Groundwater (µg/L)</td>
<td>0.52-4.1</td>
<td>0.08-0.13</td>
<td>0.02-0.02</td>
<td>0.02-0.02</td>
<td>0.21-1.32</td>
<td>0.01-0.1</td>
<td>0.03-0.05</td>
<td>0.33-6.73</td>
<td>2.24-75.24</td>
</tr>
<tr>
<td>River water (µg/L)</td>
<td>4.30-57.4</td>
<td>0.90-21.0</td>
<td>0.07-0.17</td>
<td>0.60-6.30</td>
<td>3.61-13.40</td>
<td>0.09-0.24</td>
<td>2.16-3.99</td>
<td>1.0-17.3</td>
<td>29.0-92.0</td>
</tr>
<tr>
<td>Acid mine water (mg/L)</td>
<td>293.0</td>
<td>0.52</td>
<td>0.05-110.0</td>
<td>1.0-500.0</td>
<td>3.2-223.0</td>
<td>0.10-4.00</td>
<td>0.71-1.20</td>
<td>0.08-216</td>
<td>11.5-630.0</td>
</tr>
</tbody>
</table>

It is difficult to quantify the total amount of metals entering the environment accurately because of the limited information available. However, Pacyna and Pacyna, (2001) presented a global inventory of the natural and anthropogenic emissions of trace metals to the atmosphere. A selection of these is presented in Table 1.2.

**Table 1.2:** Global inventory of natural and anthropogenic emissions (tonnes / year) of trace metals to the atmosphere in 1995. (Source: Pacyna and Pacyna 2001)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Anthropogenic emissions</th>
<th>Natural emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>18000</td>
<td>12000</td>
</tr>
<tr>
<td>Cd</td>
<td>76000</td>
<td>13000</td>
</tr>
<tr>
<td>Cr</td>
<td>147000</td>
<td>44000</td>
</tr>
<tr>
<td>Cu</td>
<td>35000</td>
<td>28000</td>
</tr>
<tr>
<td>Hg</td>
<td>22000</td>
<td>25000</td>
</tr>
<tr>
<td>Mn</td>
<td>11000</td>
<td>317000</td>
</tr>
<tr>
<td>Ni</td>
<td>95000</td>
<td>30000</td>
</tr>
<tr>
<td>Pb</td>
<td>119300</td>
<td>12000</td>
</tr>
<tr>
<td>Zn</td>
<td>57000</td>
<td>45000</td>
</tr>
</tbody>
</table>

1.2.1.1 Sources of aluminium

Aluminium is a naturally occurring metal found in surface and groundwater due to geochemical weathering processes (Gensemer and Playle, 1999). The mobilisation from soils and rocks by acidic rain has also been associated with high concentrations of aluminium found in some rivers and lakes (Wren and Stephenson, 1991; Pyrzynska *et al.*, 1999). The use of chemical coagulants in water treatment processes e.g. Al$_2$(SO$_4$)$_3$ can also significantly increase the aluminium concentrations in treated drinking water (Driscoll and Lettermann, 1988).
1.2.1.2 Sources of copper

The quantity of copper entering the environment is not accurately known and annual estimates range from 11,000 million metric tonnes (Nriagu, 1979) to 1.8 million metric tonnes (National Academy of Science Report, 1977). Most of this is deposited in soils and surface waters by atmospheric deposition (Pacyna and Pacyna, 2001). Atmospheric copper mainly comes from the production of non-ferrous metals and the combustion of fossil fuels (Table 1.3). The largest natural sources are windblown dusts, sea salt sprays, volcanic emissions and decaying vegetation (Nriagu 1979).

The inputs of copper to natural waters have increased considerably during the last century due to the leaching of wood preservatives, corrosion of anti-fouling paints and the increase in domestic and industrial waste discharges (Nriagu, 1979).

Table 1.3: Global emissions (tonnes / year) of copper, mercury, lead and zinc to the atmosphere from anthropogenic activities. (Source: Pacyna and Pacyna 2001)

<table>
<thead>
<tr>
<th>Source</th>
<th>Cu(II)</th>
<th>Hg(II)</th>
<th>Pb(II)</th>
<th>Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion of fuels (stationary sources)</td>
<td>7081</td>
<td>1475</td>
<td>11690</td>
<td>9417</td>
</tr>
<tr>
<td>Pig and iron steel production</td>
<td>142</td>
<td>29</td>
<td>2926</td>
<td>2118</td>
</tr>
<tr>
<td>Cement production</td>
<td>-</td>
<td>133</td>
<td>268</td>
<td>2670</td>
</tr>
<tr>
<td>Municipal waste</td>
<td>547</td>
<td>107</td>
<td>771</td>
<td>1563</td>
</tr>
<tr>
<td>Sewage sludge incineration</td>
<td>74</td>
<td>2</td>
<td>50</td>
<td>370</td>
</tr>
<tr>
<td>Primary non-ferrous metal production</td>
<td>17709</td>
<td>164</td>
<td>14610</td>
<td>40343</td>
</tr>
<tr>
<td>Secondary non-ferrous metal production</td>
<td>162</td>
<td>-</td>
<td>205</td>
<td>529</td>
</tr>
</tbody>
</table>
According to Pacyna and Pacyna (2001), anthropogenic inputs to the environment are now two to five times higher than the natural loadings. The major source of copper in industrial effluents comes from metal plating baths, boiler pipes, and production of primary non-ferrous metals (Table 1.3). In commercial scale mining areas, atmospheric deposition is the major source of copper in surface water (US EPA 1980). Typical copper concentrations of various industrial and municipal waste streams are shown in Table 1.4.

Table 1.4: Copper concentrations of industrial and municipal waste streams

<table>
<thead>
<tr>
<th>Source</th>
<th>Concentration (mg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid mine drainage</td>
<td>223.0</td>
<td>Tabak et al., 2003</td>
</tr>
<tr>
<td>Electroplating rinse water</td>
<td>31.0</td>
<td>Christensen and Delwiche, 1982</td>
</tr>
<tr>
<td>Silver plating</td>
<td>3.0-900.0</td>
<td>Dib and Makhloufi, 2004</td>
</tr>
<tr>
<td>Hospital wastewater</td>
<td>0.1</td>
<td>Emmanuel et al., 2005</td>
</tr>
<tr>
<td>Domestic wastewater</td>
<td>0.1-0.3</td>
<td>Rule et al., 2006</td>
</tr>
<tr>
<td>Light industrial wastewater</td>
<td>0.1-0.5</td>
<td>Rule et al., 2006</td>
</tr>
</tbody>
</table>

1.2.1.3 Sources of Mercury

Mercury is one of the least abundant metals found at the Earth’s crust and enters surface waters by out-gassing from ocean vents and atmospheric deposition from volcanic emissions (Pyle and Mather, 2003). Mercury enters the terrestrial environment by the breakdown of minerals in soils and rocks and exposure to wind and water (Elder, 1988).

Anthropogenic sources include industrial discharges (Harada, 1995), emissions from coal fired power stations (Pavlish et al., 2003) and the application of agrochemicals (Smith, 1995). The largest mercury emitter countries are listed in Table 1.5.
Table 1.5: Mercury released to the environment from fossil fuel combustion (Source: Pacyna and Pacyna, 2001)

<table>
<thead>
<tr>
<th>Number ranking</th>
<th>Country</th>
<th>Emissions (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>China</td>
<td>495</td>
</tr>
<tr>
<td>2</td>
<td>India</td>
<td>117</td>
</tr>
<tr>
<td>3</td>
<td>Australia</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td>Zaire</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>United States</td>
<td>77</td>
</tr>
<tr>
<td>6</td>
<td>South Africa</td>
<td>76</td>
</tr>
<tr>
<td>7</td>
<td>Russia</td>
<td>54</td>
</tr>
<tr>
<td>8</td>
<td>Japan</td>
<td>45</td>
</tr>
<tr>
<td>9</td>
<td>Korea</td>
<td>44</td>
</tr>
<tr>
<td>10</td>
<td>Kazakhstan</td>
<td>36</td>
</tr>
</tbody>
</table>

In the atmosphere mercury is widely dispersed in gaseous and particulate forms and may circulate for years, accounting for its widespread global distribution (Pyle and Mather, 2003). Therefore, atmospheric deposition is the major source of mercury in terrestrial and aquatic environments (Pacyna and Pacyna 2001; Yang and Rose, 2003). Anthropogenic activities can release mercury directly into soils and groundwater e.g. application of agricultural fertilisers (Foster and Charlesworth, 1996), scrap metal recycling (Jensen et al., 2000) and industrial waste water (Holt, 2000). Mercury concentrations of some industrial and municipal waste streams are shown in Table 1.6.
Table 1.6: Mercury concentrations in various industrial and municipal waste streams

<table>
<thead>
<tr>
<th>Source</th>
<th>Concentration (mg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloro-alkali plant waste</td>
<td>315.0-340.0</td>
<td>Ferreira and De-Carvalho, 1997</td>
</tr>
<tr>
<td>Petrochemical industry</td>
<td>2.8</td>
<td>Campanella et al., 1986</td>
</tr>
<tr>
<td>Pharmaceutical wastewater</td>
<td>3.8</td>
<td>Cyr et al., 2002</td>
</tr>
<tr>
<td>Hospital wastewater</td>
<td>5 x 10^{-4}</td>
<td>Emmanuel et al., 2005</td>
</tr>
<tr>
<td>Domestic wastewater</td>
<td>2 x 10^{-3}-2 x 10^{-4}</td>
<td>Rule et al., 2006</td>
</tr>
<tr>
<td>Light industrial wastewater</td>
<td>2 x 10^{-4}</td>
<td>Rule et al., 2006</td>
</tr>
</tbody>
</table>

1.2.1.4 Sources of Lead

Lead is found in the Earths crust as a constituent of the minerals galena (PbS), angelside (PbSO₄) and cerusite (PbCO₃) (US EPA Consumer fact-sheet). The most important natural emission of lead to the atmosphere is from wind blow dust (Elder, 1988).

Table 1.7: Global emissions of lead from automobiles (Source: Pacyna et al., 1995)

<table>
<thead>
<tr>
<th>Continent</th>
<th>Minimum (tonnes / yr)</th>
<th>Maximum (tonnes / yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe</td>
<td>19507</td>
<td>19507</td>
</tr>
<tr>
<td>Africa</td>
<td>6852</td>
<td>11992</td>
</tr>
<tr>
<td>Asia</td>
<td>32996</td>
<td>44293</td>
</tr>
<tr>
<td>North America</td>
<td>10414</td>
<td>15780</td>
</tr>
<tr>
<td>South America</td>
<td>4866</td>
<td>7270</td>
</tr>
<tr>
<td>Australia</td>
<td>2000</td>
<td>2000</td>
</tr>
</tbody>
</table>
Combustion of fossil fuels accounts for the largest anthropogenic emissions into the environment (Table 1.7). Other major inputs are the production of non-ferrous metals, iron and steel production (Pacyna et al., 2001). Corrosion of lead-based paints and metal recycling releases lead into surface water (Holt, 2000), while lead in groundwater comes from scrap metal recycling and industrial discharges (Jensen et al., 2000; Pacyna and Pacyna, 2000).

Dissolved lead is mainly present in the inorganic form (Pb\(^{2+}\)) but can also be in tetravalent forms such as alkyl leads (Besser et al., 2001). Until recently a major source of lead in drinking water was from the corrosion of the solder used in copper plumbing systems (Goyer, 1993). Also, sporting activities such as fishing and wildfowling can deposit significant quantities of lead in aquatic and terrestrial environments (Pain, 1991). Lead concentrations from various industrial and municipal waste streams are shown in Table 1.8.

**Table 1.8**: Lead in various industrial and urban waste streams

<table>
<thead>
<tr>
<th>Source</th>
<th>Concentration (mg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid mine drainage</td>
<td>1.2</td>
<td>Lin et al., 2006</td>
</tr>
<tr>
<td>Hospital wastewater</td>
<td>3.5 x 10(^{-3})</td>
<td>Emmanuel et al., 2005</td>
</tr>
<tr>
<td>Domestic wastewater</td>
<td>1 x 10(^{-3})-2 x 10(^{-2})</td>
<td>Rule et al., 2006</td>
</tr>
<tr>
<td>Light industrial wastewater</td>
<td>9 x 10(^{-3})-4 x 10(^{-2})</td>
<td>Rule et al., 2006</td>
</tr>
</tbody>
</table>
1.2.1.5 Sources of Zinc

Zinc is abundant in the earths crust and occurs naturally in soil and water by physical and chemical weathering of igneous and metamorphic rocks (Elder, 1988). According to Elinder (1986), global production of zinc increased from 0.5 million tonnes in 1900 to 6.1 million tonnes in 1978. Consequently more zinc has entered the environment and become widely distributed. The concentrations of zinc found in some industrial and municipal waste streams are shown in Table 1.9.

**Table 1.9: Concentrations of zinc in industrial and municipal waste streams**

<table>
<thead>
<tr>
<th>Source</th>
<th>Concentration (mg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid mine drainage</td>
<td>630.0</td>
<td>Tabak et al., 2003</td>
</tr>
<tr>
<td>Electroplating rinse water</td>
<td>28.0</td>
<td>Christensen and Delwiche, 1982</td>
</tr>
<tr>
<td>Hospital wastewater</td>
<td>0.5</td>
<td>Emmanuel et al., 2005</td>
</tr>
<tr>
<td>Domestic wastewater</td>
<td>0.3-0.7</td>
<td>Rule et al., 2006</td>
</tr>
<tr>
<td>Light industrial wastewater</td>
<td>0.1-0.5</td>
<td>Rule et al., 2006</td>
</tr>
</tbody>
</table>

The major natural and anthropogenic sources and pathways of aluminium, copper, mercury, lead and zinc into the aquatic environment are summarised Table 1.10.
Table 1.10: Natural and anthropogenic sources of metals in aqueous environments

<table>
<thead>
<tr>
<th>Sources</th>
<th>Metals</th>
<th>Pathways</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Natural</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atmospheric deposition</td>
<td>Al(III), Cu(II), Hg(II), Pb(II), Zn(II)</td>
<td>Precipitation and leaching from soils</td>
<td>Tipping et al., 2003</td>
</tr>
<tr>
<td>Bio-chemical activity</td>
<td>Al(III), Cu(II), Hg(II), Fe(III)</td>
<td>Soils, rivers</td>
<td>Sposito, 1989</td>
</tr>
<tr>
<td>Geological weathering</td>
<td>Al(III), Cu(II), Pb(II), Zn(III)</td>
<td>Soils, rivers</td>
<td>Elder, 1988</td>
</tr>
<tr>
<td>Volcanic emissions</td>
<td>Al(III), Hg(II), Pb(II)</td>
<td>Atmospheric deposition</td>
<td>Pyle and Mather, 2003</td>
</tr>
<tr>
<td>Storm water run off</td>
<td>Cd(II), Cu(II), Hg(II), Pb(II)</td>
<td>Rivers and drains</td>
<td>Blake et al., 2003</td>
</tr>
<tr>
<td><strong>Anthropogenic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agrochemicals</td>
<td>Cu(II), Hg(II), Zn(II)</td>
<td>Soil run off</td>
<td>Edwards et al., 1990</td>
</tr>
<tr>
<td>Automobiles</td>
<td>Cd(II), Hg(II), Pb(II)</td>
<td>Atmospheric deposition</td>
<td>Pacyna and Pacyna, 2001</td>
</tr>
<tr>
<td>Domestic wastewater</td>
<td>Cu(II), Hg(II), Zn(II)</td>
<td>Rivers</td>
<td>Ericsson et al., 2002</td>
</tr>
<tr>
<td>Coal power plants</td>
<td>Cu(II), Hg(II), Pb(II), Zn(II)</td>
<td>Atmospheric deposition</td>
<td>Pavlish et al., 2003</td>
</tr>
<tr>
<td>Mining</td>
<td>Cu(II), Hg(II), Zn(II)</td>
<td>Atmosphere</td>
<td>Santos et al., 2004</td>
</tr>
<tr>
<td>Chemical emissions</td>
<td>Cu(II), Hg(II), Pb(II), Zn(II)</td>
<td>Atmospheric deposition</td>
<td>Holt, 2000</td>
</tr>
<tr>
<td>Shooting and fishing</td>
<td>Pb(II)</td>
<td>Soils, sediments, surface water</td>
<td>Pain, 1991</td>
</tr>
<tr>
<td>Metal recycling</td>
<td>Cu(II), Cd(II), Pb(II)</td>
<td>Surface leaching to groundwater</td>
<td>Jensen et al., 2000</td>
</tr>
<tr>
<td>Sewage</td>
<td>Cu(II), Hg(II), Pb(II), Zn(II)</td>
<td>Rivers</td>
<td>Yoshizaki and Tomida, 2000</td>
</tr>
</tbody>
</table>
1.2.2 Metal sinks

Soils, vegetation and surface waters are effective sinks for pollutants, including metals (Yang and Rose, 2003; Pulford and Watson, 2003). Ice sheets can provide a detailed history of natural and anthropogenic pollution events (Macdonald and Fyfe, 2005).

1.2.2.1 Soils

Soils (particularly peats) are effective sinks for a large range of metals (Nicholson et al., 2003; Shotyk et al., 2003). However, the mobility and bioavailability of metals in soils is dependant on physio-chemical characteristics such as drainage, cation exchange capacity and the pH (Sposito, 1989; Tipping et al., 2003). Estuarine sediments are also effective sinks for pollutants and contain large quantities of trace metals bound in anoxic zones (Gambrell, 1994; Williams et al., 1994). Consequently, the bioavailability and mobility of metals is greatly reduced compared to well oxidised soils (Brady, 1990). Estuarine vegetation and sediments are such effective sinks they are used extensively for the stabilisation of metal effluents (Bryan and Langston, 1992; Weis and Weis, 2004).

1.2.2.2 Vegetation sinks

Terrestrial and aquatic flora can be effective bio-accumulators of metals because of their active and passive circulation of elements (Pulford and Watson, 2003, Martins et al., 2004). Metals deposited onto plants are either adsorbed or flushed into the soil by precipitation (Gambrell, 1994). Some species (e.g. lichens) can even accumulate radioactive metals with no adverse metabolic effects (Haas et al., 1998; Purvis et al., 2004; Golubev et al., 2005).
1.2.2.3 Marine sinks

Oceans cover approximately 75% of the Earth’s surface and provide a large surface area for the deposition of metals (Trujillo and Thurman 2005). A specific example is the sea-surface micro layer, where lipids, fatty acids and proteins are effective sinks for pollutants and have an important role in their global distribution (Wurl and Oubbard, 2004). However, most of the metals deposited in oceans sink to the sea bed and are partitioned into ocean sediments, where retention times can be millions of years (Eisler, 2000).

1.2.3 Metal toxicity

Exposure to elevated levels of metals can have serious health threats in both environmental and occupational settings (Chang, 1998 and Hu, 2000). Although copper and zinc are essential micro-nutrients, an excess of non-essential metals e.g. mercury and lead can lead to acute toxicity symptoms or death (Harada, 1995; Graeme and Pollack 1998). The toxicity and bioavailability of dissolved metals varies and largely depends on the pH, metal type, concentration and water hardness (Wren and Stephenson, 1991; Koukal et al., 2003).

As most organisms obtain their nutrients from the soil, vegetation and water, metals can be bio-accumulated and bio-magnified through the food chain (Harada, 1995; Langdon et al., 2003; 2004; Endo et al., 2005).

However, it is well beyond the scope of this thesis to cover all aspects associated with metal toxicity in great detail. Therefore, the eco-toxicological effects of the main metals investigated in these studies are briefly discussed in the following sections.
1.2.3.1 Toxic Effects of Aluminium

The association between aluminium in drinking water, pre-senile dementia and Alzheimer’s disease has been frequently reported (Srinivasen et al., 1999). As early as 1942, Kopeloff et al. (1942) and later Klatzo et al. (1965) observed the onset of neuro-pathological diseases in animals exposed to low levels of aluminium. A regional study conducted by Martyn et al. (1989) concluded that the rate of Alzheimer’s disease in humans was 1.5 times higher where the aluminium concentration in drinking water exceeded 0.11 mg/L compared to regions with < 0.01 mg/L.

Conversely, a report by the Australian National Environmental Health Forum (1998) proposes that there is still insufficient evidence to suggest that aluminium in drinking water is a significant contributor towards Alzheimer’s disease. More recently, a comprehensive review by Gupta et al. (2005) reported that the neurotoxic effects of aluminium are beyond any doubt. The current Maximum Contaminant Level (MCL) for aluminium in drinking water is 0.2 mg/L. (US EPA 2006).

1.2.3.2 Toxic effects of Copper

Copper is an essential micro-nutrient required for proper enzyme production and function (Campbell, 1990). Insufficient amounts can lead to iron deficiencies while excessive doses can cause liver damage and anaemia (Garrick et al., 2003). The most toxic form of copper is the cuprous ion (Cu⁺), because of the easy mobility across the blood brain barrier (Eisler, 1998). There is also growing epidemiological evidence that suggests copper is toxic for humans, with the increasing incidences of cancer reported among coppersmiths (Leonard et al., 2004).
Copper toxicity is pH dependant and several studies have shown it becomes more toxic to freshwater fish at acidic pH values (Wren and Stephenson, 1991; Clearwater et al., 2002). Copper is also phytotoxic and is used effectively as an algicide to control algal blooms and prevent unwanted marine growth on ships hulls (Konstantinou and Albanis, 2004). The MCL for copper in drinking water is 2.0 and 1.3 mg/L for the EU 2006 and US EPA 2006 respectively.

1.2.3.3 Toxic Effects of Lead

Lead is highly toxic to humans, flora and fauna with cumulative and non-degradative characteristics (Tong et al., 2000). Lead has been used extensively by humans since prehistoric times and has become widely distributed within the environment (Gilfillan, 1965). Consequently, the exposure to and uptake of lead has increased bringing significant health and environmental implications (Pain, 1991; Guinee et al., 1999).

High levels of lead ingested into the body causes damage to the brain, kidneys, nervous system and the red blood cells (Johnson, 1998). The US EPA considers lead to be highly toxic and a major health and environmental threat (US EPA metal toxicity profiles). Chronic lead exposure is a particular concern for infant children exposed to low levels via contaminated drinking water or passed over in their mother’s milk (Goyer, 1993; Johnson, 1998). The MCL for lead in drinking water is 0.005 and 0.0015 mg/L for the EU 2006 and US EPA 2006 respectively.
1.2.3.4 Toxic Effects of Mercury

When considering environmental impact, three forms of mercury are important, elemental mercury Hg$^0$, divalent mercury Hg$^{2+}$ and methyl mercury CH$_3$Hg$^{3+}$ (Boening, 2000). The most bio-available forms are elemental and organic mercury (Quig, 1998). Methyl mercury is highly toxic and is easily adsorbed and bio-accumulated by many aquatic organisms (Naimo, 1995; Endo et al., 2005). Mercury vapour and organomercury compounds (e.g. alkyl mercury) can readily enter the central nervous system and are highly neurotoxic (Chang, 1998). A recent study has shown that mercury can even be neurotoxic at the low levels of exposure found in dental surgeries (Hu, 2000). The MCL for mercury in drinking water is 0.002 mg/L for the EU 2006 and US EPA 2006.

1.2.3.5 Toxic Effects of Zinc

Zinc is an essential micro-nutrient required for the structure and function of insulin structure (Campbell, 1990). In aquatic systems, zinc tends to be partitioned into the sediment and is less frequently found as hydrated zinc ions and organic and inorganic complexes (Koukal et al., 2003). Zinc is not generally perceived to be a serious risk to human health (US EPA Guidelines). In fact, zinc is now being used as a less toxic alternative to the organotin compounds in algal biocides (Konstantinou and Albanis, 2004).

However, zinc is phytotoxic and limits have been imposed for the application of sewage sludge’s and agrochemicals containing zinc to agricultural land (86/278/EEC). The MCL for zinc in drinking water is 5.0 mg/L for the EU and US EPA 2006.
1.3. ENVIRONMENTAL RELEVANCE

Safe water is an essential commodity for the well being of all life on earth and the preservation of our natural environment (WHO Guidelines 2005). Therefore, the prevention of aquatic pollution is one of the biggest challenges facing mankind.

1.3.1 Water pollution control

The modern history of pollution control started in the UK with the Rivers Pollution Prevention Act 1876. This act imposed a total ban on any form of pollution. However, this type of legislation proved to be totally unworkable (Ball and Bell, 1995). Following this was the National Rivers Authority (NRA) and the (Prevention of Pollution Act 1951), where consent was required for industrial or sewage discharges into most inland waters.

The next major advancement in the UK was the Control of Pollution Act 1974, which extended geographical boundaries to include underground, tidal and coastal waters out to the three mile limit. This act also provided public registers of information and made the provision for private prosecutions. However, enforcement of any new environmental legislation relied on commencement orders and these were not applied for until the mid 1980s. The delay in application was mainly due to the costs associated with upgrading under performing sewage works operated by the local authorities (Ball and Bell, 1995).

The main legislation introduced for control of metal pollution in the UK was the Environmental Protection Act Part 1 1990 (Control of Dangerous Substances), the Water Industry Act and the Prescribed Processes and Substances Regulations (1991).
1.3.1.1 The World Health Organization

The World Health Organization (WHO) produced a set of guidelines for drinking-water quality in 1984. These are now regarded as the international reference used for standards setting. The guidelines were revised again in 1988 based on a consultation period spent reviewing the latest scientific research on the toxicity and eco-toxicity of dissolved metals and metal speciation.

1.3.1.2 The EU and Water Pollution

Over the years there have been increasing demands from environmental organisations and the general public for cleaner rivers and lakes, groundwater and coastal beaches. To address these issues, the European Commission has made the protection and enhancement of our natural water resources one of its priorities.

European water quality legislation started in 1975 by setting of quality standards for rivers and lakes used for drinking water abstraction and culminated in 1980 by setting binding quality targets for our drinking water (Chave, 2001). It also included objective legislation on fish waters, shellfish waters, bathing waters and groundwater. The EU Water Framework Directive (EUWFD) will be the operational tool setting the objectives for water quality and protection well into the next century (Chave, 2001).

Metal pollution within the EUWFD is controlled under the Dangerous Substances Directive (76/464/EEC). This separates metals into two lists. The black list covers metals so toxic, persistent or bio accumulative that priority is given to eliminating them e.g. cadmium and mercury. The grey lists covers metals with some environmental risks but are considered less harmful e.g. chromium, copper, lead, nickel and zinc.
The discharge limits for the black list metals into the environment are further regulated by “Daughter Directives” relating to:

- Mercury discharges by the chloro-alkili electrolysis industry (82/176/EEC)
- Mercury discharges from other industries (84/156/EEC)
- Cadmium and its compounds (85/513/EEC)

In 1998 the European Union drew up the Council Directive for the quality of water intended for human consumption (98/83/EEC). This was adapted from the earlier Directive (80/778/EEC) and based on the latest scientific knowledge that was used for the revision of the WHO guidelines. The amended Directive also provides a sound basis for providers and consumers of drinking water throughout the EU (Chave, 2001). Table 1.11 shows the earlier EU Directives and the recently amended designations introduced.

**Table 1.11: Designated and amended EC Water Quality Directives**

<table>
<thead>
<tr>
<th>Designations</th>
<th>Directive categories</th>
<th>*Amended designations</th>
</tr>
</thead>
<tbody>
<tr>
<td>76/464/EEC</td>
<td>Dangerous substances discharges (List I and II)</td>
<td>80/68/EEC &amp; 2000/60/EC</td>
</tr>
<tr>
<td>80/68/EEC</td>
<td>Protection of groundwater</td>
<td></td>
</tr>
<tr>
<td>91/271/EEC</td>
<td>Urban waste water treatment</td>
<td>98/15/EEC</td>
</tr>
<tr>
<td>98/83/EEC</td>
<td>Drinking water quality</td>
<td></td>
</tr>
<tr>
<td>2000/60/EEC</td>
<td>River basin management</td>
<td></td>
</tr>
</tbody>
</table>

**Specific designations**

<table>
<thead>
<tr>
<th>Designations</th>
<th>Directive categories</th>
<th>*Amended designations</th>
</tr>
</thead>
<tbody>
<tr>
<td>82/176/EEC</td>
<td>Mercury discharges chloro-alkali electrolysis industries</td>
<td></td>
</tr>
<tr>
<td>84/156/EEC</td>
<td>Mercury discharges other industries</td>
<td></td>
</tr>
<tr>
<td>83/513/EEC</td>
<td>Cadmium discharges from industry</td>
<td></td>
</tr>
<tr>
<td>84/491/EEC</td>
<td>Discharges of hexachlorocyclohexane</td>
<td></td>
</tr>
<tr>
<td>86/280/EEC</td>
<td>Certain dangerous substances (List I)</td>
<td>88/347/EEC and 90/415/EEC</td>
</tr>
</tbody>
</table>

**Sources:** [http://ec.europa.eu/environment/water/water-dangersub/76_464.htm](http://ec.europa.eu/environment/water/water-dangersub/76_464.htm) [accessed 19/03/07]

1.3.1.3 WATER QUALITY STANDARDS

Table 1.12 lists a summary of the maximum concentration limits (MCLs) for metals in drinking water imposed by the World Health Organisation, United States Environmental Protection Agency (US EPA) and the European Union.

Table 1.12: Maximum Contaminant Levels (MCLs) for metals in drinking water (mg/L).

<table>
<thead>
<tr>
<th>Metal</th>
<th>WHO a</th>
<th>US EPA b</th>
<th>EU Directives c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>0.2</td>
<td>0.5-2.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.003</td>
<td>0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.05</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Copper</td>
<td>1.0</td>
<td>1.3</td>
<td>2</td>
</tr>
<tr>
<td>Lead</td>
<td>0.01</td>
<td>0.015</td>
<td>0.01</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.001</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.07</td>
<td>no guideline</td>
<td>no guideline</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.02</td>
<td>0.1</td>
<td>0.02</td>
</tr>
<tr>
<td>Silver</td>
<td>0.1</td>
<td>0.01</td>
<td>no guideline</td>
</tr>
<tr>
<td>Uranium</td>
<td>0.002</td>
<td>0.003</td>
<td>0.002*</td>
</tr>
<tr>
<td>Zinc</td>
<td>5.0</td>
<td>5.0</td>
<td>No guideline</td>
</tr>
</tbody>
</table>

Notes: * = Under review: Source Information:

bUnited States Environmental Protection Agency (US EPA) [online] Drinking water contaminants and their maximum contaminant levels. Available from: [http://www.epa.gov/safewater/mcl.html] [17/09/05]

Comparative Table for WHO and EU Water Quality Regulations [online] Available from: [http://www.lenntech.com/WHO-EU-water-standards.htm] [20/03/07]
1.4. WATER TREATMENT PROCESSES

To comply with water quality regulations, potable water and industrial wastewater contaminated with metals must be effectively treated. The type of treatment will depend on the physio-chemical characteristics of the water, metal type and the final concentration required for discharge to receiving waters. A range of conventional and highly specialised options are available (Tels, 1987; Eccles, 1995). The following sections aim to provide a brief overview of the main physical, chemical and emerging biological processes.

1.4.1 Physical processes

1.4.1.1 Sand filtration

Sand filtration is one of the oldest known processes for the purification of potable water (Baker, 1981). Slow Sand Filtration (SSF) has been used for over two centuries in settings as varied as London and the Highlands of Peru (Weber et al., 1997). The low cost and ease of operation makes sand filters attractive options for small rural communities and developing nations (US EPA Technical brief, 2000).

Their original application was for the removal of suspended solids, primarily for aesthetic purposes (Simpson, 1827). But with the advent of germ theory, removal of microbial pathogens became their primary function (Rideal, 1902). In fact, before chemical treatments were available e.g. chlorination, SSF was the principal defence against water borne diseases (Frankland, 1886). However, their full potential was restricted then by the limited knowledge of the mechanisms that controlled particle and pathogen removal (Ellis, 1985). Therefore, the design and progress of sand filters evolved slowly, as extensive pilot studies were necessary for each new application (Newcomer, 1991).
Research interest was resurrected in 1990 when the US EPA began to evaluate SSFs to meet new drinking water quality regulations (Pontius, 1990, Theis et al., 1992). More recently, there has been growing interest in sand filters for the removal of metals and organics (Benjamin et al., 1996). Innovative new developments have shown that sand coated with metal oxides (e.g. Fe(OH)$_3$) are highly efficient adsorbents for metals and metal complexes (Lo et al., 1997; Muhamed et al., 2000; Vaishya and Gupta, 2003).

Lai and Chen (2000, 2001) conducted column studies using iron oxide coated sands for the removal of copper, lead and humic materials. They concluded that complete removal of both metals and humics were achieved before breakthrough. In addition, the recovery of metals and regeneration of the column was possible. The development of modified sands for the removal of metals and organics from potable and industrial wastewater continues to evolve (Han et al., 2006a and b). For the interested reader, a table providing further examples with associated references is given in the CD ROM attached (see Appendix 2A Table 1a).

The proposed metal removal mechanism with iron oxide coated sands is shown in (Figure 1.1), where Me$^{2+}$ represents a divalent transition metal.

![Figure 1.1: Mechanism for the adsorption of metals onto iron oxide coated sand.](image)
1.4.2 Chemical processes

Chemical treatments of metal bearing water can convert metals into less hazardous forms and the by-products treated and disposed of safely. In addition, if strategic metals (e.g. chromium, gold, silver and zinc) are recovered and recycled, the overall costs can be offset (Jha et al., 2001; Kentish and Stevens, 2001). There are four main chemical treatment processes for the removal of metals. These are listed below and shown schematically in Figure 1.2.

- Chemical precipitation / neutralisation
- Electrochemical recovery
- Solvent extraction / membrane separation
- Adsorption / ion exchange and chelating resins

Figure 1.2: Chemical treatments for the removal of metals (Adapted from Rorrer, 1998)
1.4.2.1 Chemical precipitation

Chemical precipitation is a widely used and proven process (US EPA Water Technology Fact Sheet 2000). By controlled adjustment of pH (or neutralisation), dissolved metal ions react with a chemical precipitant to form insoluble precipitates. Typical precipitants are sodium hydroxide, calcium hydroxide, sodium carbonate, sodium sulphide, and sodium borohydride (Andrus, 2000). The precipitated solids (or sludge’s) are then removed by a combination of coagulation, flocculation, sedimentation or filtration.

The overall chemical reactions for the precipitants discussed above are shown in equations 1.1-1.5. Where, $M^{2+}$ represents a divalent metal (Rorrer, 1998)

\[
\begin{align*}
M^{2+} (aq) + 2 \text{NaOH} & \rightarrow M (OH)_2(s) + 2\text{Na}^+ (aq) \quad (1.1) \\
M^{2+} (aq) + \text{Ca(OH)}_2 & \rightarrow M (OH)_2(s) + \text{Ca}^{2+} (aq) \quad (1.2) \\
M^{2+} (aq) + \text{Na}_2\text{S} & \rightarrow MS (s) + 2\text{Na}^+ (aq) \quad (1.3) \\
M^{2+} (aq) + \text{Na}_2\text{CO}_3 & \rightarrow M \text{CO}_3(s) + 2\text{Na}^+ (aq) \quad (1.4) \\
4 M^{2+} (aq) + \text{NaBH}_4 + 8 \text{NaOH} & \rightarrow 4 M^0 + \text{NaBO}_2 + 8\text{Na}^+ + 6\text{H}_2\text{O} \quad (1.5)
\end{align*}
\]

The solubility limits (pH for minimum solubility), chemical consumption and sludge characteristics vary depending on effluent composition, metal type and precipitant used. For example, chromium is a good candidate for hydroxide precipitation, as the minimum solubility of ($\text{CrOH}_3$) begins around (pH ~ 6.5) and remains stable up to pH 11 (Rorrer, 1998). Conversely, hydroxide precipitation is less effective for lead as the solubility limit is not reached until a pH $\geq$ 10. Therefore, sodium carbonate is the preferred precipitant for lead (Tels, 1987). The pH and minimum solubility limits for some typical metals (using NaOH) are listed in the Appendix (see Appendix A Table 1.1a).
Sulphide precipitants, for example Na₂S or NaHS, applied under comparable conditions to hydroxides generally have lower solubility limits, better removal efficiencies and smaller sludge volumes (Tels, 1987). However, the formation of hydrogen sulphide gas (H₂S) and oxidation to soluble sulphates are potential disadvantages. Chemicals consumption, manual labour and disposal of metal enriched sludge’s are the main costs associated with chemical precipitation. Advantages of chemical precipitation are its well established and in some cases metals can be reduced to < 1 mg/L (Andrus, 2000).

1.4.2.2 Coagulation

Chemical precipitation is often combined with coagulation (e.g. addition of Al₂(SO₄)₃ or FeCl₃ salts (Poon and Choo, 1999). Coagulants neutralise negatively charged colloids suspended in solution and facilitate the formation of larger aggregates (Masters, 1998). Chitin and chitosan are potential substitutes, as these long chain polysaccharides act as bridges between suspended particles forming larger aggregates (or flocs). This improves the sedimentation rates, filtration, dewatering and produces biodegradable sludges (Kawamura, 1991; Pan et al, 1999).

1.4.2.3 Flocculation

Flocculation often follows on from coagulation. This is a gentle stirring stage where the suspended precipitates attract colloidal particles and form larger more stable flocs (Masters, 1998).
1.4.2.4 Sedimentation and filtration

Following flocculation, the treated water flows through a sedimentation tank or clarifier large enough to retain the water long enough for suspended solids to settle out. Typical retention times range from 1 to 10 hours (Masters, 1998). The sludge that collects in sedimentation tanks can either be removed manually by flushing out or continuously cleaned by a mechanically operated scraper. Treated effluent from the tank can then be passed through a sand filter if required. The overall process is shown in Figure 1.3.

![Figure 1.3: Overall unit process for chemical precipitation, coagulation, flocculation and sedimentation (Adapted from Masters, 1998)](image)

1.4.2.5 Electrochemical recovery

Electrochemical recovery includes electrowinning, electrodialysis and cementation. All processes make use of externally applied electric potential to separate or plate out dissolved metals. Electrowinning plates metals onto the cathode side of an electrolytic cell, electrodialysis separates metals by diffusion across a selectively permeable membrane located between the anolyte and catholyte sides of electrochemical cell (Tels, 1987). These processes can be combined for specific applications. For example, the circuit board industry uses a combination of electrowinning and electrodialysis to recover high purity copper, regenerate and recycle etching fluid (Rorrer, 1998).
1.4.2.6 Cementation

Cementation involves a replacement reaction by deposition of a target metal onto a sacrificial metal of higher oxidation potential (Tels, 1987). Cementation of copper onto iron is a classical example and has been used for centuries on a commercial scale to produce copper from waste mine water (Lung, 1986). The overall chemical reaction is shown by Equation 1.6.

\[ \text{Cu}^{2+} (\text{aq}) + \text{Fe}^0 (\text{s}) \rightarrow \text{Cu}^0 (\text{s}) + \text{Fe}^{2+} \]  

(1.6)

In wastewater treatment, cementation is used effectively to remove highly toxic metals and replace them by less toxic sacrificial metals (e.g. iron, copper or zinc). For example, Ku et al., (2002) reported that >99.9% of Hg(II) could be removed from acidic solutions in less than 30 minutes by cementation onto zinc powder. Cementation is also an important process in hydrometallurgical engineering for the recovery and recycling of valuable and strategic metals (Jha et al., 2001). According to Sulka and Jaskula (2004), effective recovery of high purity silver from sulphuric acid leachates can be achieved by cementation onto copper. Conversely, Hiskey and Lee (2003) observed the rate of gold deposition onto copper discs follows a first-order kinetic reaction and forms nodular Au-Cu alloys instead of pure gold.

The advantages of electrochemical recovery processes are they are well established and high purity metals can be recovered and recycled with minimal chemical requirements. Comprehensive reviews of electrochemical processes for recovery of metals from industrial wastewater were reported by (Grimm et al., 1998; Chen, 2004).
1.4.2.7 Solvent extraction and liquid membranes

Solvent extraction and liquid membranes basically perform the same function by transferring metal ions from the aqueous phase to another phase (Grimm, 1998). With solvent extraction, a non-polar solvent containing a complexing agent (e.g. EDTA) is brought into contact with a waste stream and metals selectively transfer (extraction phase). The metal enriched EDTA is then contacted with a stripping solvent (e.g. HCl) and the concentrated metal solution can be recycled back into the process stream (Rorrer, 1998). The overall unit process is shown schematically in Figure 1.4.

![Figure 1.4](image-url)

**Figure 1.4:** Removal of metals by solvent extraction (Adapted from Rorrer, 1998)

With liquid membrane separation, a solid physical barrier, selectively permeable for metals ions (the membrane), sits between the two phases. Solvent extraction and liquid membranes are well established processes and can be highly efficient if the metal concentrations and flow rates are high (Croll, 1992). However, they become uneconomic at low metal concentrations (<0.5 mg/L). An informative review of the recent developments and innovations in solvent extraction and liquid membrane technologies was given by Kentish and Stevens, (2001).
1.4.2.8 Adsorption

Throughout history carbon or forms of carbon (e.g. charcoal) have been used as adsorbents for the purification of water (Harrison, 1995). The charred-tree Moses cast into the bitter water at Marah to make it “sweet” for the Israelites to drink is thought to have functioned as an adsorbent (Old Testament, Exodus 15: 23-25). These days, activated carbons are used for removal of organics, odours, tastes and metals from domestic and industrial wastewater (Fornwalt and Hutchins, 1996).

Carbonaceous materials are heated under anaerobic conditions (300-500°C) to produce charcoal and tar. The charred material is then heated with steam or carbon dioxide to >1000 °C, which removes everything but carbon (Saha et al., 2001). The resultant product has a delicate porous structure that is nearly pure carbon, which is crushed to a powder and mixed with binders to form granules of specific size ranges. The size and distribution of the macro and micro pores are key features for effective adsorption, as they determine the ions or molecules that can be adsorbed (Sollars et al., 2001). Chemicals or gases can be added during the activation process (e.g. HNO₃, CO₂ or N₂) to produce carbons with the specific functionality to bind cationic metals (Streat et al., 2001).

The large surface areas of activated carbons are fundamental for their effectiveness to sorb contaminants. Typical surface areas of commercial carbons range from 600-1500 m²/g (Darco® Technical Sheets). Depending on the application, activated carbons are used in powdered (<150µm) or granular form (>250-2000µm). Granular carbon is the preferred choice in water treatment facilities, as it can be regenerated and used in multiple sorption-desorption cycles. While powdered carbon is used for point-of-use (POU) drinking water systems, due to large surface area to volume ratio and it takes up less space.
Recently a large range of agricultural and industrial wastes have been converted to activated carbons and shown to have potential for the removal of metals from aqueous solutions. A selection of typical materials tested is provided in the CD ROM that accompanies the thesis (see Appendix A2, Table 1.2a).

1.4.2.9 Ion-Exchange

The use of ion-exchange processes for water purification was documented as early as 330 BC, when Aristotle observed that seawater loses its salt when percolated through sand (Arden, 1968). The materials responsible for this were later shown to be naturally occurring alumino-silicates or zeolites (Sposito, 1989). Aluminium silicates were among the first materials used as ion exchangers for the softening of industrial water (Arden, 1968). However, they were unstable in acidic solutions and it was not possible to have exchanges involving hydrogen ions (H⁺) until acid resistant materials were developed (Masters, 1998). This was achieved with a degree of success recently using sulphonated coal (Brown et al., 2000).

Nowadays, ion-exchangers, consist of synthetic polymers with specific functional groups to give resins selective properties (Kiefer and Holl, 2001; Neagu et al., 2003). Using special techniques, resins can be made into porous beads, gels and foams depending on the end applications (Lawson and Hay, 1994). Chelation ion-exchange resins contain functional groups with a higher degree of metal selectivity e.g. amines, pyridines, oximines, hydroxylamines, Schiff bases and thiols (Dow Technical Notes, 2006).

Ion-exchangers require displacement reactions shown in Equations 1.7 and 1.8:

Where R represents the ligand-ion exchange site and M²⁺ a divalent metal ion.
2 R \cdot H + M^{2+} (aq) \Leftrightarrow R_2M (s) + 2 H^+ (aq) \quad (1.7)

2 R \cdot Na + M^{2+} (aq) \Leftrightarrow R_2M (s) + 2 Na^+ (aq) \quad (1.8)

Ion-exchange and chelation resins are well developed and advances in the chemistry continue to evolve (Neagu et al., 2003; Wang and Wang, 2005). A review of the history and development of ion exchange resins is given by (Abrams and Millar, 1997).

The most common process for metal removal is the packed-bed column with sorption desorption cycles. In the sorption cycle, the waste stream (influent) is delivered to a column packed with ion-exchange resin beads (Figure 1.5). The ratio of influent flow-rate to bed volume is carefully controlled so the effluent concentration remains below a predetermined target (normally the discharge limit). As the stream passes through the column, metal concentration decreases as a function of time until all exchange sites are occupied (saturation). Typical saturation capacities of commercial ion-exchange resins are 1-5 milli-equivalents (meq) of metal ion per 1ml of resin, depending on the resin and target metal (Dow Technical Data Sheets 2006).

\[ \text{Figure 1.5: Packed bed ion-exchange column. (Adapted from Rorrer, 1998).} \]
At saturation point, the stream is diverted to a fresh resin bed (column 2) and the metal loaded resin is stripped and regenerated (Figure 1.5). Regenerating solutions contain a high concentration of exchangeable ions that displaces the metals e.g. hydrogen (H\(^+\)) ions (1 M HCl) or sodium (Na\(^+\)) ions (1 M NaCl). Other regenerant solutions may be used and this largely depends on the type of resin and mechanism of metal binding. During the regeneration cycle, exchangeable ions are loaded onto the resin and metals are eluted at high concentrations. The concentrated metal solutions recovered can then be recycled or electro chemically processed to recover the metals. A selection of commonly used commercial ion-exchange resins are listed in the Appendix (see Appendix A, Table 1.3a).

Table 1.13 lists a summary of the chemical treatments presented in this Chapter with the main advantages and disadvantages of each process.

Table 1.13: Summary of chemical processes for the removal of metals

<table>
<thead>
<tr>
<th>Process</th>
<th>Chemical Energy input</th>
<th>Metal Reclamation</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical precipitation</td>
<td>Precipitant, acid and base handling</td>
<td>Metal sludge</td>
<td>Well established and proven</td>
<td>Chemical requirements, sludge disposal</td>
</tr>
<tr>
<td>Electrolytic recovery</td>
<td>Electrical power</td>
<td>Solid metal scrap</td>
<td>Pure metal recovery, no chemical consumption</td>
<td>Energy inputs, inefficient at low metal concentrations</td>
</tr>
<tr>
<td>Liquid membranes</td>
<td>Extractant solvents, fluid handling</td>
<td>Concentrated metal stream</td>
<td>Selective, continuous metal recycle</td>
<td>Durability and membrane fouling with organics</td>
</tr>
<tr>
<td>Liquid-liquid extraction</td>
<td>Extraction solvents, fluid handling</td>
<td>Concentrated soluble metal stream</td>
<td>Selective, continuous metal solution recycle</td>
<td>Capital costs, emissions to air/water, solvent disposal</td>
</tr>
<tr>
<td>Activated carbons</td>
<td>Replacement of sorbent, fluid handling</td>
<td>Metals immobilised on solid adsorbent</td>
<td>Can be effective at low concentrations</td>
<td>Selectivity disposal of material</td>
</tr>
<tr>
<td>Ion-exchange adsorption</td>
<td>Regenerant solutions and fluid handling</td>
<td>Concentrated metal ion stream</td>
<td>Selective, effective at low concentrations</td>
<td>Chemical regeneration, organic fouling</td>
</tr>
</tbody>
</table>
1.4.3 Biological processes

The main biological processes for removing metals from aqueous media are bio-precipitation, phyto-remediation, bioaccumulation and biosorption (Figure 1.6). However, it is not the objective of this thesis to cover these in detail. Therefore, the following sections will provide a brief overview with the main focus on biosorption processes.

![Figure 1.6: Biological processes for the removal of metals. (Adapted from Rorrer, 1998)](image)

The development of new and novel treatments is driven by the introduction of stricter water quality regulations (EC Water Framework Directives). However, any new process must show advantages over existing treatments. In particular, low maintenance and capital costs, better removal efficiencies and selectivity at low metal concentrations and a reduction in the toxic wastes produced (Volesky, 1994). Bioremediation processes using biosorption or bio-accumulation have been proposed as cost-effective alternatives (Atkinson et al., 1998; Bailey et al., 1999; Viera et al., 2000).
1.4.3.1 Bio-precipitation

Bio-precipitation makes use of micro-organisms (e.g. bacteria, yeasts and fungi) that reduce metal ions to an insoluble state via redox reactions (White and Gadd, 2000). Commonly used strains are the sulphate reducing bacteria *Desulfosporisinus orientis* and fungi *Aspergillus niger* that generate extra cellular hydrogen which form insoluble metal sulphides (Tabak *et al*., 2003; Malik, 2004). This bioremediation process has recently been successfully applied by Cohen (2006) to remove As(III), Cd(II) and Pb(II) from acid mine drainage waters.

1.4.3.2 Phyto-remediation

Phyto-remediation is an in-situ remediation strategy that makes use of vegetation and trees (e.g. willows and coniferous pines) to immobilise metals (Khan *et al*., 2000). This is a sustainable low cost approach and is emerging as a viable alternative to some of the conventional water treatments. Reviews providing full details of the uptake mechanisms and the advantages and disadvantages associated with these phyto-remediation processes are given by Khan *et al*., (2000), Susarla *et al*., (2002), and Pulford and Watson, (2003).

1.4.3.3 Bio-accumulation

Bio-accumulation is defined as the metabolic dependant uptake and accumulation of metals (Valdes, 2000). Any organism capable of metabolising metal ions is a potential candidate (Sag, 2001; Kadukova and Vircikova, 2005). A growing range of macro-algae, bacteria, fungi and yeasts have been patented and are now available as commercial products (Volesky, 2004; Coulibaly *et al*., 2003; Malik, 2004; Wang and Chen, 2006).
1.4.3.4 Biosorption

Biosorption is the ability of non-viable biomass to bind and concentrate metals (Stark et al., 1999; Volesky, 2003). However, because of the physio-chemical complexity of biological materials, there are many ways for metals to be sequestered. Figure 1.7 shows the major mechanisms associated with bioaccumulation and biosorption based on the classification proposed by Veglio and Beolchini, (1997).

![Figure 1.7: Metal uptake mechanisms (Veglio and Beolchini, 1997 with permission)](image)

1.5. BIOSORPTION

Biosorption is the focus of this thesis. Therefore, the main mechanisms involved with the uptake of metals are considered in more detail in the following sections and Chapters.

1.5.1 Removal mechanisms

Research is revealing that biosorption of metals occurs via a complex range of processes including chemical precipitation, physical and chemical sorption, ion-exchange, electrostatic interactions and complexation (Brady and Tobin, 1995; Wase et al., 1997;
Schneider et al., 2001; Volesky, 2003; Crini, 2005). The following sections aim to provide an overview of the main mechanisms.

1.5.1.1 Precipitation

The precipitation of metals on solid surfaces occurs more easily than in solution depending on the pH (Stumm, 1992). For example, if high concentrations of dissolved metals are present at the surfaces of biomaterials, then precipitation can occur rapidly with the formation of metal complexes (Schneider et al., 2001). However, earlier studies of metal sorption by soils and vegetation suggest it is difficult to distinguish between physical adsorption and precipitation without spectroscopic micro-analysis (Sposito, 1989).

1.5.1.2 Physical adsorption

Physical adsorption occurs when metal ions or metal complexes attach to surface binding sites (e.g. amine or carboxyl functional groups) via weak long range Van Der Waals forces and electrostatic interactions (Sparks, 2002). These mechanisms are generally non-specific in nature and reversible (Atkins, 1998). Therefore, the physical and chemical properties e.g. surface areas; particle size and chemical functionality are important considerations when selecting biosorbents.

1.5.1.3 Chemical sorption

Chemical sorption involves short range forces and the formation of strong covalent bonds (electron sharing) between specific metal binding ligands (e.g. nitrogen and sulphur atoms in chitin and protein functional groups) on the sorbent surfaces (Nieboer and
Richardson, 1980; Fourest and Roux, 1994; Brady and Tobin, 1995). This mechanism is specific and can be non-reversible (Atkins, 1998).

1.5.1.4 Ion-exchange and electrostatic attraction

Ion-exchange takes place when metal ions displace other ions during the sorption process (Sparks, 1995). The ions exchanged with biological materials during the biosorption of metals are typically hydrogen ions and the alkali and alkaline metals Na\(^+\), K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) (Da-Costa et al., 2001; Antunes et al., 2003). This is frequently proposed as the major metal removal mechanisms operating with algae, fungi and bacteria (Fourest and Roux, 1994; Kapoor and Viraraghavan, 1995; Figueira et al., 2000).

Electrostatic attraction occurs when the metal ions and sorbent surfaces are oppositely charged. The surface charge of biosorbent materials is largely dependant on the solution pH (Regine et al., 2000). For example, at neutral pH, approximately 50% of the amine groups on chitosan are protonated and available for the sorption of anions (Guibal, 2004). However, as the pH increases, the surface charge density or zeta potential becomes negative and the polymer is suitable for sorption of metal cations.

1.5.1.5 Complexation

Metal ions can bind to single ligands or through complexation or chelation with multiple ligands on biomaterials (Varma et al., 2004). For example, the biosorption of metals by fungi occur through the formation of complexes with phosphate and sulphydryl groups (Gadd, 1993). While the formation of Cu(II) complexes on chitosan occurs by chemical bonding with three oxygen atoms and one nitrogen atom from hydroxyl and amine groups (Guibal, 2004).
1.5.2 Biosorbent materials

Ongoing research has identified that a large range of natural and waste materials are suitable for the biosorption of metals. A typical selection is provided in Table 1.14.

Table 1.14: Biomaterials tested for the removal of metals from aqueous solutions

<table>
<thead>
<tr>
<th>Material</th>
<th>Country</th>
<th>Metals</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banana skins</td>
<td>Taiwan</td>
<td>Cu(II), Ni(II), Pb(II), Zn(II)</td>
<td>Annadurai et al., 2003</td>
</tr>
<tr>
<td>Cocoa shells</td>
<td>Brazil</td>
<td>Pb(II)</td>
<td>Meunier et al., 2003</td>
</tr>
<tr>
<td>Coniferous barks</td>
<td>France</td>
<td>Cu(II), Cr(III), Hg(II), Pb(II)</td>
<td>Dupont et al., 2002</td>
</tr>
<tr>
<td>Date stones</td>
<td>Israel</td>
<td>Cd(II)</td>
<td>Banat et al., 2003</td>
</tr>
<tr>
<td>Fish scales</td>
<td>Canada</td>
<td>Co(II), Pb(II), Sr(II), Zn(II)</td>
<td>Mustafiz et al., 2002</td>
</tr>
<tr>
<td>Grape stalks</td>
<td>Spain</td>
<td>Cu(II), Ni(II)</td>
<td>Villaescusa et al., 2004</td>
</tr>
<tr>
<td>Lichen</td>
<td>Turkey</td>
<td>Cu(II)</td>
<td>Fatma et al., 2006</td>
</tr>
<tr>
<td>Peat</td>
<td>Ireland</td>
<td>Cu(II), Ni(II), Pb(II)</td>
<td>Ma and Tobin, 2003</td>
</tr>
<tr>
<td>Peanut shells</td>
<td>USA</td>
<td>Cu(II)</td>
<td>Johnson et al., 2002</td>
</tr>
<tr>
<td>Plane leaves</td>
<td>Japan</td>
<td>Cr(VI)</td>
<td>Aoyama et al., 2003</td>
</tr>
<tr>
<td>Prawn shell</td>
<td>New Zealand</td>
<td>Cu(II), Pb(II)</td>
<td>Chu, 2002</td>
</tr>
<tr>
<td>Rice husks</td>
<td>Egypt</td>
<td>Cd(II), Cu(II), Mn(II), Pb(II), Zn(II)</td>
<td>Daifullah et al., 2003</td>
</tr>
<tr>
<td>Sawdust</td>
<td>France</td>
<td>Cu(II), Cd(II), Hg(II), Pb(II)</td>
<td>Marin and Ayele, 2002</td>
</tr>
<tr>
<td>Seafood wastes</td>
<td>Korea</td>
<td>Cd(II), Cu(II)</td>
<td>Lee and Allen, 2001</td>
</tr>
<tr>
<td>Seaweed</td>
<td>Canada</td>
<td>Au(II), U(II)</td>
<td>Davis and Volesky, 2003</td>
</tr>
<tr>
<td>Spent grain</td>
<td>Malaysia</td>
<td>Cd(II), Pb(II)</td>
<td>Low and Liew, 2000</td>
</tr>
<tr>
<td>Sugar beet</td>
<td>France</td>
<td>Cu(II), Ni(II)</td>
<td>Gerente et al., 2002</td>
</tr>
<tr>
<td>Wood barks</td>
<td>France</td>
<td>Cr(III), Cu(II), Pb(II), Zn(II)</td>
<td>Gloaguen and Morvan, 1997</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>China</td>
<td>Cr(VI)</td>
<td>Li et al., 2003</td>
</tr>
</tbody>
</table>
The number of materials tested as metal biosorbents has increased steadily over the last twenty years and is too extensive to be covered in this study. For the interested reader, a comprehensive list compiled from a global literature review is given in the CD ROM that accompanies the thesis (see Appendix A2, Table 1.4a Biosorbents by category).

When selecting materials as potential biosorbents, their source, availability and production costs are the main considerations (Voilesky, 1990; Daifullah et al., 2003; Babel and Kurniawan, 2003). Ideal biosorbents should be readily available in large quantities, have the right physical and chemical characteristics and be easily processed into durable granular forms (Voilesky, 1994, 2004).

A growing number of agricultural wastes are showing potential as metal biosorbents and include wood bark and sawdust (Gloaguen and Morvan, 1997; Taty-Costodes et al., 2003; Sciban and Klansja, 2004). Others include naturally abundant materials e.g. seaweeds and their derivatives, particularly the brown algae Sargassum, Ecklonia maxima, Durvillea potatorum, Laminaria hyperborea and Fucus vesiculosus which can be readily harvested from the oceans (Bailey et al., 1999; Sandlands and Edyvean, 2002; Davis et al., 2003).

While some of these materials can be effectively recycled (e.g. composted and applied to poor quality agricultural land or fed to livestock), many wastes present considerable challenges with the environmentally acceptable disposal (ADAS UK, 2006).
1.6. AIMS AND OBJECTIVES

The overall aim of this research is to evaluate naturally abundant materials and waste products for the removal of metals from aqueous solutions (e.g. to act as biosorbents). Furthermore, it is envisaged that this study will:

Contribute towards the growing body of knowledge on the metal removal mechanisms involved with biosorbent materials.

The preliminary objectives were focussed towards:

1. The process and development of raw materials; e.g. the collection, cleaning, milling and granulation to obtain a product with the desired physical characteristics.

2. Physical and chemical characterisation of materials to identify products with the optimum physico-chemical characteristics to perform as biosorbents.

3. Preliminary screening of suitable materials for the removal of copper from aqueous solutions. Key parameters investigated are contact time, metal concentration, metal type, solution pH, particle size, mass loading and conditioning of materials.

4. The most effective materials will be assessed further by comparison with commercial sorbents for copper removal and the biosorption of environmentally sensitive metals.

5. Kinetic and equilibrium modelling studies to evaluate the sorption rates and equilibrium uptake capacities of the most effective materials.
2. CHAPTER 2: MATERIALS AND METHODS
In Chapter 1, the natural and anthropogenic sources of metals, metal toxicity and the environmental issues associated with metal pollution were discussed. The conventional water treatments for the removal of metals were reviewed and the emerging biological processes introduced. In this Chapter, the selection, collection and processing of natural biosorbent materials are described and the commercial sorbents used for inter-comparison studies introduced. The analytical techniques used to physio-chemically characterise materials and the methods used to evaluate the biosorption performance are outlined.

### 2.1. INTRODUCTION

A global review of the literature revealed that the variety of materials screened as metal biosorbents has increased steadily over the last two decades (see Appendix A, Table 1.4a). Considering the number of potential candidate’s available, sourcing and developing biosorbents could easily be a time consuming and labour intensive business. However, this study will focus on local natural materials: seaweed, peat and wood products which are abundantly available and can be obtained at little or no cost.

Figure 2.1 shows that, as well as seaweeds, peat and agricultural wastes, crab carapace has recently been attracting interest as a metal biosorbent. The Highlands and Islands ports of Scotland receive some 32,000 tonnes of shellfish landed annually (Figure 2.2). A large proportion of this is the common or edible crab (*Cancer pagurus*). Only a small proportion of the crab biomass is used during processing (the meat) and the surplus (the carapace) is treated as waste and disposed of (sometimes at cost) to landfill sites. Furthermore, new EC regulations have introduced complete bans or restrictions on the disposal of untreated shellfish wastes to landfill sites (EDAS U.K, 2006).
Additional expenses can also be incurred with transportation and disposal of shellfish wastes originating from Northern and Western Islands. Thus, shellfish wastes are in plentiful supply locally and globally (Figure 2.2 and Table 2.1) and can be obtained readily (Wishart, 2003). Therefore, based on the availability of crab carapace and the natural abundance of seaweed, peat, and wood products within the study area, these materials were selected for development and screening as metal biosorbents.
Figure 2.2: Crab landings in the Highlands and Islands (metric tonnes). Source: Scottish Fisheries Statistics (2001) [http://www.scotland.gov.uk/Resource/Doc/46737/0028705.pdf]

Table 2.1: Global shellfish landings, (metric tonnes)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Crab</td>
<td>1,063,812</td>
<td>1,869,177</td>
<td>1,838,487</td>
<td>1,160,972</td>
<td>1,130,008</td>
<td>1,104,942</td>
<td>1,369,084</td>
</tr>
<tr>
<td>Lobster</td>
<td>233,867</td>
<td>217,126</td>
<td>228,942</td>
<td>227,596</td>
<td>221,749</td>
<td>224,883</td>
<td>224,074</td>
</tr>
<tr>
<td>Shrimp</td>
<td>2,631,029</td>
<td>2,736,678</td>
<td>3,026,532</td>
<td>3,076,593</td>
<td>2,940,190</td>
<td>2,942,799</td>
<td>3,523,911</td>
</tr>
</tbody>
</table>

2.2. BIOSORBENTS

2.2.1 Mechanically Milled Carapace (MMC)

Carapace from the edible crab (*Cancer pagurus*) was collected as waste from shellfish processing at Scrabster harbour, Thurso (Figure 2.2). The carapace was cleaned thoroughly with tap water, rinsed with ultra pure water (Millipore Direct Q3 Water Purification System) then air-dried overnight 20°C ± 2°C or oven dried 60 °C for 4 hours. Dry carapace was roughly broken by hand, crudely milled with a domestic food processor (Bifinett KH 525) and mechanically sieved (Retsch AS 200) to provide granular particles in the <250, 250 - 800, 800 - 2000 and >2000 µm size ranges. Processed MMC was stored in airtight containers at room temperature until use.

2.2.2 Commercially Milled Carapace (CMC)

Commercially milled carapace (*Cancer pagurus*) was obtained from Carafiltration Ltd, York, U.K. This was supplied ultrasonically cleaned and cryogenically milled at the 250-800µm size range (cost £10.0 / kg). When processed under these conditions, each particle retains its inherent macro and micro-porosity (see Chapter 3, Figure 3.1). The CMC was stored in airtight containers at room temperature until use.

2.2.3 Chitin

Commercial chitin flakes (derived from the *Cancer pagurus*) were obtained from (Aldrich, U.K). The flakes were crudely milled (Bifinett KH 525) and mechanically sieved (Retsch AS 200) to provide particles in the same size range as for MMC. Processed chitin was stored in airtight containers at room temperature until use.
2.2.4 Chitosan

Chitosan was prepared from the chitin flakes by alkaline deacetylation following the economical method proposed by Aluminar and Zainuddin, (1996). One hundred grams of chitin flakes were mixed with 2.4 L of NaOH (50% w/v) in a thermostatically controlled water bath for 5 days at a constant temperature (20 °C ± 2 °C). The resultant product was successively rinsed with ultra-pure water (Millipore Direct Q3 System) until the pH was constant then oven dried (40-60 °C) for 12 hours. The dry chitosan was crudely milled with a domestic food processor (Bifinett KH 525) and mechanically sieved (to provide particles in the same size range as for MMC. Processed chitosan was stored in airtight containers until use.

2.2.5 Seaweed

Viable and non-viable samples of the brown seaweed (Fucus vesiculosus) were harvested from inter-tidal zones of local beaches around Thurso (Figure 2.2). The seaweed was rinsed thoroughly with tap water to remove residual sand and rinsed several times with ultra-pure water. Washed seaweed was either air-dried in the laboratory at room temperature (20 °C ± 2 °C) for 24 hours or oven dried at 40°C for 6 hours. When dry the seaweed was roughly broken by hand and crudely milled using a domestic food processor (Bifinett KH 525) and mechanically sieved to provide particles in the same size ranges as for MMC. Processed seaweed was either used straight away for batch adsorption and column studies or stored in airtight containers at room temperature until required.
2.2.6 Peat

Peat was obtained from Dale and Achkeepster Farms Ltd, Causeway Mire, Caithness, U.K. The peat was either air dried at room temperature (20 °C ± 2.0 °C) or oven dried for 12 hours 60 °C. The dry peat was roughly broken using a plastic hammer and crudely milled and mechanically sieved to produce particles in the same size range as MMC. Processed peat was stored in airtight containers at room temperature until use.

2.2.7 Wood bark

Wood bark from the Douglas fir (*Psudotsuga menziesii*) was collected from wind damaged trees and forest floors around the Thurso area. The barks were rinsed with tap water until the water ran clear then rinsed with ultra-pure water. The washed barks were then air dried at room temperature (20 °C ± 2 °C) for 24 hours or oven dried at 40-60 °C for 4-6 hours. Dry barks were roughly broken by hand crudely milled (Bifinett KH 525) and mechanically sieved to provide granular particles in the same size ranges as MMC. Processed bark was stored in airtight containers at room temperature until use.

2.3. COMMERCIAL SORBENTS

2.3.1 Activated carbons

Acid-washed Darco® (granular form, 20-40 mesh size, 425-800µm) designed for general uses and Norit® (needle pellets, 2-2.8 mm length, 0.8 mm diameter) designed for use in liquid-phase adsorption systems were obtained from (Aldrich, UK). Full technical data sheets are available from: <http://www.norit-americas.com/1.2.cfm>. Both carbons were stored in airtight containers at room temperature then used as supplied.
2.3.2 Ion-exchange resin

A Dowex® 50W strongly acidic cation-exchange resin, (spherical bead form, 20-50 mesh size, 300-800µm (Aldrich, UK)) was used for these studies. This resin is 4% cross-linked with divinyl-benzene with a cation-exchange-capacity of 1.2 meq / mL. The resin was stored in airtight containers and used as supplied. Full technical data is available from: <http://www.serva.de/products/knowledge/071119.shtml>.

2.4. METHODS

2.4.1 BET surface area

2.4.1.1 Sample Preparation

Before determination of surface areas, sample surfaces were cleared of contaminants such as water and organic residues acquired from atmospheric exposure. This surface cleaning or degassing was carried out at 70 °C by passing a flowing gas mixture of nitrogen and helium (30:70) over the sample. Where helium is the carrier gas and nitrogen is the adsorbate gas. All samples were degassed for a period of 20 hours and any weight loss during this period was recorded (see Chapter 3 Table 3.2)

The specific surface areas were determined using the Brunauer, Emmet and Teller (BET) single point method (Brunauer et al., 1938). Measurements were made with a “Micromeritics” (Quantachrome Quantasorb QS10) surface area analyser using nitrogen as the adsorbate gas. This process was carried out at 70 K and atmospheric pressure. Under these conditions the area covered by each gas molecule is known to within relatively narrow limits, (e.g. 16.2 nm² for monolayer coverage of nitrogen) Langmuir (1918).
With the area covered by each gas molecule known and the volume of gas adsorbed, the surface area can be calculated using the BET equation (Equation 2.1).

\[
\frac{P}{V} (P_o - P) = \frac{1}{(V_m C)} + \frac{(C - 1) \times P}{V_m C \times P_o} \tag{2.1}
\]

Where

\( V = \) the volume of gas adsorbed at equilibrium pressure, \( P \)
\( V_m = \) the amount of gas required to give monolayer coverage
\( P_o = \) the saturated vapour pressure of the adsorptive
\( C = \) is a constant related to the heat of liquification

The BET equation theoretically gives a straight line which is limited to a narrow range of \( P / P_o \) values (0.05 – 0.30). If a plot of \( P / V (P_o - P) \) against \( P / P_o \) is linear, the slope and the intercept can be used to calculate \( V_m \) and \( C \).

These values can then be used to calculate the BET specific surface area using equation 2.2

\[
S_{\text{BET}} = \frac{V_m}{28} \times N_a \times 16.2 \times 10^{-20} \tag{2.2}
\]

Where \( N_a = \) Avagadros number and 16.2 \( \text{nm}^2 \) is the average area occupied by the adsorbate molecule (\( \text{N}_2 \)) in complete monolayer coverage.
2.4.2 Moisture content

One-gram samples (± 0.0001 g) of each processed material were placed in an oven for 4 hours at 105°C. The difference between initial mass \((M_i)\) and the final mass \((M_f)\) of materials was calculated using Equation 2.3 and expressed as a percentage moisture content. This procedure was carried out in triplicate for each material and means reported (see Chapter 3, Table 3.3).

\[
\frac{(M_i - M_f)}{M_i} \times 100
\]

(2.3)

2.4.3 Bulk densities

The bulk densities of all materials were determined following the procedure proposed by No et al. (1998). One gram of each material was placed in a 15 ml tapered graduated centrifuge tube and packed gently by tapping the tube 10 times on the bench top. The volume was recorded and the bulk density expressed in grams per millilitre (g/ml). This procedure was carried out in triplicate and the means reported.

2.4.4 SEM-EDAX analysis

2.4.4.1 Sample preparation

All materials were prepared by mounting samples of the required particle size onto carbon adhesive discs on pin type SEM stubs. These were then sputter coated with a conductive layer (~ 20 nm) of Gold and Palladium.
2.4.4.2 SEM-EDAX elemental mapping and imaging

Samples were embedded in a low viscosity epoxy resin by vacuum impregnation. The resin was cured for 48 hours, ground with silicon / carbon discs and sputter coated with ~ 20 nm of vacuum evaporated Carbon. Surface micro-structures of materials were examined using a Phillips XL 20 Scanning Electron Microscope at 20 kV using either the secondary electron or back scattered electron emission signals. Qualitative SEM-EDAX microanalysis and X-ray elemental mapping was done with an Oxford Be EXL II micro-analyser fitted with a beryllium, silicon / lithium crystal spectrometer.

2.4.5 Carbon Hydrogen and Nitrogen analysis

Elemental analysis for the carbon (C), hydrogen (H), and nitrogen (N) content of selected materials were performed using a (Carlo-Ebra NA 2500) elemental analyser calibrated with acetanilide standards.

2.4.6 Metal solutions

All metal salts and chemical reagents used were of analytical grade (Aldrich U.K). Stock solutions of metals were prepared (at the required concentrations, mg/L or mol/L) by dissolving the appropriate amount of LiCl, KCl, CaCl₂, CdCl₂, CuSO₄, HgCl₂, MgCl₂, NaCl, NiCl₂, and Pb(NO₃)₂ and ZnCl₂ in ultra-pure water (Millipore Direct Q3 System). Ultra-pure water was also used for all dilutions and the preparation of standard solutions for instrument calibrations. Stock metal solutions were acidified (pH ~2) by the addition of 1.0 M HCl and stored in the fridge until use.
2.4.7 pH measurements and control

All pH measurements were taken with a Jenway 3340 ion-meter. The instrument was calibrated twice daily or before each set of new measurements with buffer solutions of pH 4.0, 7.0 and 9.2. Selected batch adsorption studies were conducted with the pH controlled between 4.3 and 4.7 to determine the removal of metals by sorption and precipitation processes. In these studies, any pH adjustments required were made by the drop-wise addition of 1.0 M HCl or 1.0 M NaOH.

2.4.8 Biosorption performance

2.4.8.1 Batch adsorption studies

The metal sorption efficiency of materials was evaluated using batch adsorption studies carried out at room temperature (T 22 °C ± 2 °C) by mechanically agitating on an orbital shaker (IKA KS 260). Measured amounts of materials were contacted with 100 ml metal solutions at the initial concentration (C_i) and pH (pH_i) and agitated at 350 rpm for the required contact time. The resultant mixtures were vacuum filtered (Whatman GF/A 1.6µm pore size) and the final pH (pH_f) recorded. Filtrate solutions were acidified (pH ~ 2) and stored under refrigeration until analysis. All batch studies were done in triplicate and the means reported.

2.4.8.2 Column Studies

Flow through column studies were performed (in the down-flow mode) using a sintered glass column (20 cm in length, internal diameter 2 cm). Single metal solutions of 500 mg/L were delivered at a constant flow rate (6.4 ml/min) to 20 grams of MMC of the 250-800µm size fraction. Effluent samples were collected at 15-minute intervals, the pH
recorded then vacuum filtered (Whatman GF/A 1.6µm pore size). Filtered solutions were acidified with 1.0 M HCl to pH ~ 2 and stored under refrigeration until analysis.

2.4.9 Metal analysis

Dissolved Cd$^{2+}$, Cu$^{2+}$, Hg$^{2+}$, Mg$^{2+}$, Ni$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ concentrations were analysed using a Perkin-Elmer Atomic Absorption Spectrophotometer (Laboratory Instruments Incorporated., Model 357) with an air-acetylene flame. The full operational parameters are given in Appendix B (see Table 2.1a). Dissolved Na$^+$, K$^+$, Li$^+$ and Ca$^{2+}$ concentrations were analysed using a Sherwood Flame Photometer (Model No 410). All working standards were prepared by diluting 1000 mg/L stock solution with ultra-pure water. All measurements recorded in triplicate and the means presented.

2.4.9.1 Metal removal efficiencies

The removal efficiencies of all sorbents were determined with Equation 2.4.

$$\text{Efficiency} = \frac{(C_i - C_f)}{C_i} \times 100 \tag{2.4}$$

The metal uptake, q (mg metal/gram sorbent) was calculated using Equation 2.5

$$q = \frac{V \left( C_i - C_f \right)}{M} \tag{2.5}$$

Where $V$ = the volume of solution (L), $C_i$ = initial concentration (mg/L or mmols) $C_f$ = final concentration (mg/L or mmols) and $M$ = the dry weight of sorbent (g)

Any materials or methods different from those described above are introduced in subsequent chapters.
3. CHAPTER 3 CHARACTERISATION OF MATERIALS
In Chapter 2, the collection and processing of natural materials and the analytical methods used to evaluate the performance as metal biosorbents were discussed. The production of crab chitosan from chitin was summarised and the commercial metal sorbents used for inter-comparison studies introduced. This Chapter presents results from the basic physical and chemical analysis of the natural and commercial adsorbents to identify products with the desired characteristics to perform as metal biosorbents.

3.1. INTRODUCTION

Many studies have shown the potential of low cost biomass for the removal of metals from aqueous media (Bailey et al., 1999; Wase and Forster, 1997; Gupta et al., 2000). However, only materials with the right physical and chemical characteristics make them practical and cost effective for use in industrial scale applications Volesky, (2004). The ideal physical and chemical properties required for optimum biosorption performance include; structural and mechanical stability, porosity, large surface areas, hydrophilicity and metal binding functional groups (Volesky, 1994; Atkinson et al., 1998; Bakkaloglu et al., 1998; Davis et al., 2003).

Therefore, the aim of this Chapter was to establish the bulk densities, micro structures, BET surface areas, moisture contents, and carbon, hydrogen and nitrogen content of materials to identify candidates for biosorption screening studies. This analysis was conducted for CMC, MMC, Fucus vesiculosus, chitin, chitosan, peat and Douglas fir wood bark (Pseudotsuga menziesii) of the 250-800µm size fraction and MMC at 250-800 and 800-1500 µm size fractions (Table 3.1). For comparison, the same characterisation was done for commercial activated carbons Darco® and Norit® and Dowex® 50W strongly acidic ion-exchange-resin beads.
3.2. METHODS

- BET surface areas (e.g. external and internal area) were determined following the method proposed by Bruneaur et al. (1939). (See Chapter 2, section 2.4.1)

- Moisture contents and dry weight bulk densities were determined following the methods proposed by No et al. (1998). (See Chapter 2, sections 2.4.2 and 2.4.3)

- Scanning Electron Microscopy (SEM) was used to examine the surface microstructures of all materials. (See Chapter 2, section 2.4.4)

- Carbon, Hydrogen and Nitrogen contents. (See Chapter 2, section 2.4.5).

Table 3.1: Summary of the physical and chemical analysis of materials.

<table>
<thead>
<tr>
<th>Material (and particle sizes)</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET surface area</td>
</tr>
<tr>
<td>Natural MMC (250-800µm)</td>
<td>✓</td>
</tr>
<tr>
<td>Natural MMC (800-2000µm)</td>
<td>✓</td>
</tr>
<tr>
<td>Natural MMC* (250-800µm)</td>
<td>✓</td>
</tr>
<tr>
<td>Natural CMC (250-800µm)</td>
<td>✓</td>
</tr>
<tr>
<td>Natural CMC (800-1500µm)</td>
<td>✓</td>
</tr>
<tr>
<td>Natural Chitin (250-800µm)</td>
<td>✓</td>
</tr>
<tr>
<td>Natural Chitosan (250-800µm)</td>
<td>✓</td>
</tr>
<tr>
<td>Natural Fucus vesiculosus (250-800µm)</td>
<td>✓</td>
</tr>
<tr>
<td>Natural Peat (250-800µm)</td>
<td>✓</td>
</tr>
<tr>
<td>Natural Wood bark (250-800µm)</td>
<td>ND</td>
</tr>
<tr>
<td>Natural Darco® (425-800µm)</td>
<td>✓</td>
</tr>
<tr>
<td>Natural Norit® (2.8mm L, 0.8mm D)</td>
<td>✓</td>
</tr>
<tr>
<td>Natural Dowex® (300-800µm)</td>
<td>✓</td>
</tr>
</tbody>
</table>

Notes: MMC* agitated with 1000 mg/L Cu(II) for 4 hours, ND = Not determined
3.3. RESULTS AND DISCUSSION

3.3.1 BET surface areas

The weight loss during the degassing cleaning process (Chapter 2 section 2.4.1.1) and the BET specific surface areas of each of the materials evaluated in this study are presented in Table 3.2.

Table 3.2: BET surface areas of natural materials and commercial adsorbents

<table>
<thead>
<tr>
<th>Material</th>
<th>Degassing (hrs)</th>
<th>Weight loss (%)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMC (250-800µm)</td>
<td>20</td>
<td>3.7</td>
<td>22.5</td>
</tr>
<tr>
<td>MMC (800-2000µm)</td>
<td>20</td>
<td>3.7</td>
<td>21.5</td>
</tr>
<tr>
<td>MMC (250-800µm)</td>
<td>20</td>
<td>4.5</td>
<td>22.8</td>
</tr>
<tr>
<td>CMC (250-800µm)</td>
<td>20</td>
<td>3.0</td>
<td>33.4</td>
</tr>
<tr>
<td>CMC (800-1500µm)</td>
<td>20</td>
<td>2.5</td>
<td>30.5</td>
</tr>
<tr>
<td>Chitin (250-800µm)</td>
<td>20</td>
<td>3.8</td>
<td>3.9</td>
</tr>
<tr>
<td>Chitosan (250-800µm)</td>
<td>20</td>
<td>12.2</td>
<td>6.0</td>
</tr>
<tr>
<td>Fucus vesiculosus (250-800µm)</td>
<td>20</td>
<td>3.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Peat (250-800µm)</td>
<td>ND</td>
<td>ND</td>
<td>32.5*</td>
</tr>
<tr>
<td>Wood bark (250-800µm)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Darco® (425-800µm)</td>
<td>20</td>
<td>&lt; 0.1</td>
<td>455</td>
</tr>
<tr>
<td>Norit® (2.8mm L, 0.8mm D)</td>
<td>20</td>
<td>2.4</td>
<td>780.0</td>
</tr>
<tr>
<td>Dowex® (300-800µm)</td>
<td>20</td>
<td>57.0</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Notes: *MMC contacted with 1000 mg/L Cu(II) solution for 4 hours. (*Allen et al., 2004)

CMC, MMC, chitin, Fucus vesiculosus and Norit® all had a small weight loss during the degassing period (2.4 - 4.5 %). The lower weight loss for CMC with respect to MMC and chitin was attributed to the ultrasonic cleaning removing loose surface debris (see Chapter 2, section 2.2.2). The larger weight loss from the chitosan particles (12.2 %)
can be attributed to surface debris and residual moisture remaining from the deacetylation process. The smallest weight loss was recorded for Darco® (< 0.1 %) and is probably the result of the acid washing pre-treatment (see Chapter 2 section 2.3.1). The largest weight loss was observed for the Dowex® resin beads (57.0 %) and is due to adsorption of moisture from the beads by the dry nitrogen gas.

CMC particles have larger surface areas (~33.0 %) than MMC particles of a similar size (Table 3.2). This can be attributed to the cryogenic milling, which preserves the macro and micro porosity (Chapter 2 section 2.2.2 and Figure 3.3.3). The slightly larger surface area of MMC particles contacted with 1000 mg/L Cu solution (22.8 m²/g), may be due to micro precipitates in pore voids increasing internal surface area. Chitin and chitosan have smaller surface areas (6.0 and 3.9 m²/g respectively) than MMC and CMC. These are consistent with those reported in the literature and are the result of reduced porosity (No et al., 1998). Fucus vesiculosus has the smallest surface area (0.19 m²/g) and is consistent with those of other seaweeds using the same method (e.g. 0.22, 0.18 and 0.19 m²/g for Fucus serratus, Ascophyllum nodosum and Laminaria digitata respectively.

Commercial activated carbons Darco® and Norit® have the largest surface areas, 455 and 780 m²/g respectively (Table 3.2). The surface areas of commercial carbons depend largely on the physical and or chemical activation methods and the precursor materials (Johns et al., 1999; Sollars et al., 2001). Darco® and Norit® are produced from lignite and activated with CO₂ or steam which produces carbons with extensive porosity and accounts for the larger surface areas (Aldrich Technical Notes 2005). Dowex® resin beads have a small BET surface area (0.02 m²/g) because of the low porosity and structure collapse during degassing.
3.3.2 Moisture content and bulk densities

The moisture content and bulk densities of (raw undried) natural and commercial adsorbents are shown in Table 3.3.

Table 3.3: Moisture content and bulk densities of natural and commercial sorbents

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle size (µm)</th>
<th>Moisture content* (%)</th>
<th>Bulk density* (g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMC 250-800</td>
<td>250-800</td>
<td>2.77</td>
<td>0.67</td>
</tr>
<tr>
<td>MMC 800-2000</td>
<td>800-2000</td>
<td>3.23</td>
<td>1.32</td>
</tr>
<tr>
<td>CMC 250-800</td>
<td>250-800</td>
<td>1.20</td>
<td>0.79</td>
</tr>
<tr>
<td>CMC 800-1500</td>
<td>800-1500</td>
<td>4.78</td>
<td>1.49</td>
</tr>
<tr>
<td>chitin</td>
<td>250-800</td>
<td>6.50</td>
<td>3.51</td>
</tr>
<tr>
<td>chitosan</td>
<td>250-800</td>
<td>16.91</td>
<td>4.05</td>
</tr>
<tr>
<td><em>Fucus vesiculosus</em></td>
<td>250-800</td>
<td>12.34</td>
<td>1.42</td>
</tr>
<tr>
<td>Peat</td>
<td>250-800</td>
<td>12.76</td>
<td>ND</td>
</tr>
<tr>
<td>Wood bark</td>
<td>250-800</td>
<td>14.39</td>
<td>3.15</td>
</tr>
<tr>
<td>Darco®</td>
<td>425-800</td>
<td>9.06</td>
<td>0.37</td>
</tr>
<tr>
<td>Norit®</td>
<td>2.8mm L, 0.8mm D</td>
<td>3.46</td>
<td>0.34</td>
</tr>
<tr>
<td>Dowex®</td>
<td>300-800</td>
<td>63.66</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Notes: *All measurements in triplicate and the means presented; ND = Not determined
MMC, CMC and chitin have lower moisture contents (1.2-6.5 %) and smaller bulk densities (0.67-1.49 g/ml) than the other natural materials. This is due to the large mineral (CaCO₃) and chitin content of crab carapace. Chitin has a rigid crystalline structure that imparts hydrophobic qualities and provides structural and mechanical stability to crustacean shells (Welinder, 1975; Tokura and Nishi, 1978).

Chitosan, *Fucus vesiculosus* and Douglas fir wood bark have higher moisture contents (12.3-16.9 %) and larger bulk densities (1.42-4.25 g/ml) because of their large open pore structures and low mineral contents (see Figures 3.2, 3.3 and 3.4). Consequently, this imparts hydrophilic qualities and adsorption of water is less restricted. Although the *Fucus vesiculosus* has a low bulk density at the dry weight tested, previous studies revealed that particles of the same size swelled on contact with water increasing the bulk volume significantly.

Commercial carbons Darco® and Norit® have moisture contents of 9.06 and 3.46 % respectively. The higher moisture content observed for Darco® is probably due to prolonged exposure to the atmosphere prior to analysis. Both the carbons have small bulk densities, 0.37 and 0.34 g/ml respectively. This is the result of the high density of the precursor materials, thermal and chemical treatments during the activation process and their intended applications for water purification (See Darco® and Norit® Technical data sheets).

Dowex® resin beads have the highest moisture content of all the materials tested (63.6 %). This is because of the resinous nature and elastic properties of the beads which are designed to shrink and swell. This is also consistent with the moisture contents given by the manufacturers (Dow Technical data sheets 2005).
3.3.3 SEM-EDAX micro-analysis

3.3.3.1 Natural materials

Figure 3.1 shows the SEM microstructures of MMC and CMC.

![SEM micrographs of MMC and CMC](image)

**Figure 3.1**: SEM micrographs of MMC and CMC (250-800 µm particle size)

Although the micro-structures of CMC and MMC particles are compact, both exhibit macro and micro-porosity (Figure 3.1a and b). Hegdahl *et al.* (1977a, b and c) reported the abundance of pore canals (150,000-220,000 mm²) permeating the cuticle layers of carapace from the *Cancer pagurus*. This could account for the extensive micro porosity and larger BET surface areas of CMC and MMC with respect to chitin and chitosan (Table 3.2).
Figure 3.2: SEM micrographs of chitin and chitosan flakes (250-800 µm particle size)

Chitin particles have ribbed surfaces with a complex array of sheets and folds (Figure 3.2 a). They also show a less compact and more fibrous structure than MMC and CMC with large macro-pores and some micro-pores distributed over the surfaces (Figure 3.2 b). This is due to demineralisation by HCl removing CaCO₃ and exposing chitin fibres during extraction from crab-shell (No et al., 1998; No and Meyers, 2000).

Chitosan has a more open pore structure with large macro-pores distributed evenly over the surfaces (Figure 3.2 c and d). This would account for the smaller BET surface area, higher moisture content and larger bulk density with respect to MMC, CMC and chitin (Table 3.2).
The *Fucus vesiculosus* particles have flat plate like external structures with little or no surface micro-porosity (Figure 3.3a and d). This could account for the small BET surface area of this seaweed due to the restriction of nitrogen to internal pores (Table 3.2). However, the internal structure of a damaged particle shows a highly porous network of cylinder or tube like voids with a large variation in pore sizes (Figure 3.3 b, c and d). This sponge like internal structure would account for the significant swelling properties and increase of bulk volume when the seaweed particles are contacted with water.

**Figure 3.3**: SEM micrographs of seaweed *Fucus vesiculosus* (250-800 µm particle size)
The micro-structure of the Douglas fir wood barks shows an undulating flaky topography with a large number of sheets and folds protruding from the surfaces (Figure 3.4 a, b). There is extensive porosity in the form of macro and micro-pores connected by a continuous network of vertical tubes and column-like channels (Figure 3.4 c, d). There are also a number of smaller micro-pores distributed unevenly over the surfaces and connecting to the macro pores (Figure 3.4). This morphology would impart hydrophilic properties and would account for the larger moisture content observed. Given the extensive macro and micro-porosity of the wood bark, it would be interesting to know how the BET surface area compares with the other materials.
Figure 3.5: SEM micrographs of peat (250-800 µm particle size)

The peat micro surfaces show a large number of triangular and rectangular shaped blocks distributed in patches over the surface (Figure 3.5 b, c). There are also a large number of macro and micro-pores distributed unevenly over the surfaces. Peat is a complex material comprising of cellulose, humic, fulvic acids and contains many different types of plants depending on where it is formed. This extensive porosity and complex array of surface features may account for the relatively large surface area of this natural material (Allen et al., 2004).
3.3.3.2 Commercial adsorbents

**Figure 3.6:** SEM micrographs of Darco® activated carbon (particle size 425-800 µm)

Darco® activated carbon exhibits extensive porosity with a random distribution of macro and micro-pores over the surfaces ranging in size from 2-30 µm (Figure 3.6). This high density of pores is probably due to the thermal pre-treatment and activation method (Blazewicz et al., 1999) and accounts for the larger BET surface area with respect to the natural materials. The carbon surfaces and internal pores appear to be relatively free from surface debris (Figure 3.6 c and d). This is due to the acid washing pre-treatment of the lignite precursor material (Darco Technical Data sheets).
The Norit® activated carbon needle pellets show a more compact and closed microstructure compared with the Darco® granules (Figure 3.7). This can be explained by the lower thermal temperature and the activation method used for the production of this carbon (Darco® Technical Data Notes). This treatment results in a high density of micro-pores evenly distributed over the external and internal surfaces of the material. This would also account for the considerably larger BET surface area of this activated carbon with respect to Darco® (Table 3.2).
Dowex® 50W ion-exchange resin beads have a smooth spherical external structure with negligible macro or micro porosity detected at the magnifications used (Figure 3.8 a). This would account for the small BET surface area recorded for this material (Table 3.2). The large surface cracks seen in (Figure 3.8 b) are the result of shrinkage of the beads caused by heat treatment to remove moisture prior to SEM-EDAX analysis.

Figure 3.8: SEM micrographs of Dowex® 50 W cation exchange resin beads
3.3.4 Carbon, hydrogen and nitrogen analysis

Table 3.4 shows the percentage Carbon (C), Hydrogen (H) and Nitrogen (N) content of selected natural materials.

Table 3.4: Carbon, hydrogen and nitrogen content of selected natural materials

<table>
<thead>
<tr>
<th>Material</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMC (250-800µm)</td>
<td>15.10</td>
<td>1.70</td>
<td>1.10</td>
</tr>
<tr>
<td>CMC (250-800µm)</td>
<td>11.40</td>
<td>1.50</td>
<td>1.30</td>
</tr>
<tr>
<td>Chitin (250-800µm)</td>
<td>46.72</td>
<td>6.70</td>
<td>4.50</td>
</tr>
<tr>
<td>Chitosan (250-800µm)</td>
<td>32.41</td>
<td>5.10</td>
<td>5.97</td>
</tr>
<tr>
<td><em>Fucus vesiculosus</em> (250-800µm)</td>
<td>35.19</td>
<td>5.31</td>
<td>1.32</td>
</tr>
<tr>
<td>Peat (250-800µm)</td>
<td>60.10</td>
<td>7.43</td>
<td>0.92</td>
</tr>
</tbody>
</table>

MMC and CMC have smaller C and H contents compared to all the other materials because of the high inorganic mineral content. These results are consistent with those reported for crab carapace in the literature (An et al., 2001). Chitin and chitosan have a higher C and H contents than MMC and CMC due to demineralisation by acid during extraction from crab carapace. Chitin and chitosan have a higher N content (emboldened values) than the other materials indicating the larger proportion of amine functional groups. These groups are significant for biosorbents as they act as chelation sites and are responsible for the uptake of metals by chitin rich materials (Eiden et al., 1980; Guibal, 2004; Varma et al., 2004).

The C H N contents for *Fucus vesiculosus* are consistent with those reported in the literature for other seaweeds (Gevaert et al., 2001). As expected peat have the largest carbon content of all the natural materials and the lowest nitrogen content. These results are in agreement with those reported in the literature (Allen et al., 2004).
3.4. CONCLUSIONS

There is considerable variability in the physical and chemical properties of the natural materials and commercial sorbents characterised. To summarise:

- MMC, CMC and chitin have low moisture content and bulk densities, macro and micro-porosity, relatively large surface areas and hydrophobic properties.

- Chitosan, wood bark, peat and seaweeds have higher moisture contents and bulk densities, less micro porosity, smaller surface areas and hydrophilic properties.

- Commercial carbons Darco® and Norit® are highly porous with large surface areas, low moisture contents and small bulk densities. Dowex® ion-exchange resin beads have a high moisture content, negligible porosity and small surface area.

- MMC and CMC have a small C and H content and large CaCO₃ and chitin content. This imparts structural stability and a hydrophobic quality. Chitin and chitosan have the largest N content indicating the presence of amine functional groups.

All the natural materials showed varying degrees of structural and mechanical stability, bulk densities, BET surface areas, hydrophilic and hydrophobic properties. However, a common feature of all natural materials is micro and macro- porosity and mixed chemical functionality. From a comprehensive review of the biosorption literature, these are desirable characteristics for the biosorption of metals. Therefore, MMC, CMC, *Fucus vesiculosus* and Douglas fir wood bark will be tested for the removal of metals from aqueous solutions in Chapter 4.
4. CHAPTER 4: PRELIMINARY SCREENING OF BIOMATERIALS
In Chapter 3, natural materials were physically and chemically characterised and compared with commercial sorbents to identify potential biosorbents. Brown seaweed \( (Fucus vesiculosus) \), Douglas fir wood-bark \( (Pseudotsuga menziesii) \), MMC and CMC (derived from \( Cancer pagurus \)) were all shown to have physical (e.g. surface areas and extensive porosity) and chemical properties (e.g. mixed functionality) to merit further evaluation. This Chapter presents results from preliminary screening of these materials for the removal of Cu(II) from aqueous solutions. The most promising candidates were selected for extended screening studies with a range of environmentally relevant metals.

4.1. INTRODUCTION

Metal contamination of aqueous environments presents considerable concerns due to their persistence and potential toxicity (Smith, 1999). Conventional treatment processes e.g. chemical precipitation, carbon adsorption, and ion-exchange resins can be expensive or ineffective particularly at dilute concentrations (see Chapter 1 Table 1.17). Therefore, alternative low cost solutions are urgently required. Recently, a diverse range of waste biomass and naturally abundant materials have shown potential for the removal of metals over a large concentration range (Mackay et al., 1999; Gupta et al., 2005). The metal sequestering properties of such biomass may provide an innovative and economical approach to the problem (Coughlin et al., 1990; Veglio et al., 1997).

However, only those materials with good removal efficiencies, high sorption capacities and selectivity for toxic and strategic metals are suitable for consideration in large scale biosorption processes (Volesky, 1994; Kratochvil et al., 1997; Vieira and Volesky, 2000).
Based on the results from Chapter 3, the aim of this chapter was to assess the biosorption potential of MMC, CMC, *Fucus vesiculosus* and Douglas fir wood bark for the removal of Cu(II) from aqueous solutions. The performance of each material was tested using batch adsorption studies designed to assess the effects of contact time and initial concentration (Part A). Depending on the results obtained from these studies, the most efficient materials were selected for extended investigations. Laboratory scale column trials and batch adsorption studies were used to establish the affinity and selectivity of materials for a range of environmentally relevant metals (Part B).

### 4.2. MATERIALS AND METHODS

- **Biomaterials**

  MMC, CMC, and Douglas fir wood bark were processed as described in Chapter 2 (sections 2.2.1, 2.2.2, 2.2.5 and 2.2.7). Samples of brown seaweed (*Fucus vesiculosus*) were collected fresh, rinsed with tap water and air dried for 24 hours. CMC, wood bark and seaweed were tested at the 250-800µm particle size and MMC using 250-800, 800-2000 and > 2000 µm particle sizes.

- **Metal solutions**

  Metal solutions were prepared by dissolving analytical grade LiCl, KCl, CaCl₂, CdCl₂, CuSO₄, HgCl₂, MgCl₂, NiCl₂, and Pb(NO₃)₂ and ZnCl₂ salts (Aldrich, U.K) in ultra-pure water (Millipore Direct Q3 System) as described in Chapter 2 (section 2.4.6). The chloride, sulphate and nitrate salts were chosen to represent the common background anions found in natural and wastewaters.
- Batch adsorption studies

Batch adsorption studies were conducted at room temperature (21 °C ± 2 °C) by mechanically agitating (350 rpm), 5 g fractions of each material with 100 ml of single metal solutions at the required contact time, initial metal concentration (Cᵢ) and initial pH (pHᵢ). After the required period of contact time, the solutions were vacuum-filtered acidified (pH ~2) and stored until analysis. All studies were conducted in triplicate and the means presented. If the standard deviations were >10 %, these are shown as error bars on graphs or indicated in the text and tables.

- Column studies

Column studies were performed at room temperature (21 °C ± 2 °C) with a sintered glass column in the down flow mode. Single metal solutions (500 mg/L) were delivered at a constant flow rate (6.4 ml/min) to 20 grams of MMC, 250–800µm size fraction. Effluent samples were collected at 15-minute intervals, pH recorded, vacuum filtered and stored until analysis. Figure 4.1 shows a schematic and the experimental set up.

Figure 4.1: Schematic view (a) and experimental (b) set-ups for column studies, metal solution (1), peristaltic pump (2) and effluent collection vessel (3)
• **Metals analysis**

The final concentrations of Li(I), K(I) and Na(I) in the filtrates were determined using a flame photometer (Sherwood model 410) and Ca(II), Cu(II), Zn(II), Ni(II), Mg(II), Hg(II), Cd(II) and Pb(II) using an atomic adsorption spectrophotometer (Laboratory Instruments Incorporated model 537) as described in Chapter 2 (section 2.4.9).

• **Evaluation of materials**

The metal removal efficiencies of each material were determined from the mass balance of the sorption systems using equations 2.3 and 2.4 (see Chapter 2 sections 2.4.9.1).

In **Part A**, below (materials comparison), the metal biosorption performances of each material were assessed using the percentage of Cu(II) removed (%) as a function of contact time and initial concentration.

In **Part B**, (metals comparisons), the biosorption performance of the most efficient material/s from Part A is represented by the percentage removal (%) and specific uptake of metals (q), (mg metal uptake/ g dry weight) as a function of contact time, initial metal concentrations and particle size.
4.3. RESULTS AND DISCUSSION

4.3.1 Materials comparison (Part A)

4.3.1.1 Effects of contact time

CMC, MMC, *Fucus vesiculosus* and Douglas fir bark were evaluated for the removal of Cu(II) as a function of contact time. Figure 4.2 shows percent removed at initial concentration of 500 mg/L.

![Figure 4.2](image.png)

Figure 4.2: Effects of contact time. $C_1 = 500$ mg/L, pH$_{i}$ = 4.5, V = 100 ml, T = 21 °C ± 2 °C, 5 g material, 250-800 µm size fraction, agitation rate 350 rpm.

The removal of Cu(II) was similar for all materials, with a rapid initial phase, typically 5-20 minutes, with efficiencies of 98.8, 93.0, 77.3 and 75.0% at 10 minutes for CMC, MMC, wood bark and *Fucus vesiculosus* respectively. This was followed by a much slower phase and approach to pseudo-equilibrium (20-60 minutes). In general, contact times longer than 40 minutes showed no improvement in Cu(II) removal. Therefore, 60 minutes was used as a standard time for all other studies.

The order of maximum removal was CMC>MMC>Bark>Seaweed with 99.6, 99.3, 87.5 and 80.9 % at 40, 40, 60 and 20 minutes respectively.
4.3.1.2 Effects of Concentration

CMC, MMC, *Fucus vesiculosus* and Douglas fir wood bark were evaluated for the removal of Cu(II) as function of concentration. Figure 4.3 shows the percentage removals as concentration increases from 100 to 1000 mg/L.

![Figure 4.3: Effects of initial concentration: 60 minutes contact time, pH$_i$ = 4.5, V = 100 ml, 21 °C ± 2 °C, 5 g, 250-800 µm size fraction, agitation rate 350 rpm.](image)

The Cu(II) removal efficiency by CMC was excellent over the entire concentration range (95.0-99.0 %, Figure 4.3). While MMC was highly efficient (96.3 %) up to 500 mg/L, removal decreased to 85.1 % at 1000 mg/L. Wood bark removed 93.0 % at 200 mg/L then the efficiency decreases steadily to 61.2 % at 1000 mg/L. Conversely, the efficiency of *Fucus vesiculosus* was 40.0 % at lower concentrations (100–200 mg/L) then increased steadily to 82.0 % at 1000 mg/L.

The order of maximum removal was CMC>MMC>Bark>Seaweed were 98.6, 96.7, 93.0 and 85.1 % at 1000, 200, 200 and 1000 mg/L respectively.
4.3.2 Discussion

The removal of Cu(II) by CMC and MMC was rapid and highly efficient achieving >98.0% by 20 minutes (Figure 4.2). CMC was highly efficient over the entire concentration range (Figure 4.3). While MMC was effective up to 500 mg/L, efficiency decreased to 84.5% at 1000 mg/L indicating the saturation of metal binding sites. The higher Cu(II) removal sustained by CMC with respect to MMC could be due to the larger surface area of CMC providing more metal binding sites (See Chapter 3 Table 3.2 and Figure 3.1). Similar sorption kinetics and efficiencies were reported by Evans et al. (2002) using chitosan-based carapace and by Cochrane et al. (2006) using carapace from the Cancer pagurus under comparable conditions. These results are also consistent with a comparative study by An et al. (2001). These authors demonstrated that >99.0% of the metal uptake by crab carapace (Chinonecetes opilio) occurred in the first 60 minutes and exceeded that of commercial ion-exchange resins.

Although wood-bark was less efficient than MMC and CMC at higher Cu(II) concentrations, removal was fast over the first 5 minutes (Figures 4.2 and 4.3). This supports the work of Dupont et al. (2002) who reported the highest uptake of Cu(II) by Douglas fir barks occurs in the first few minutes. The effective uptake of metals by wood barks has been attributed to rapid ion-exchanges between metals and hydrogen ions from carboxyl and phenol groups of tannin and pectin (Al-Asheh and Duvnjak, 1997).

However, a disadvantage of tannin containing materials is the discoloration of water due to leaching of soluble tannins and phenols (Randall, 1977). In these studies, tainting of water and disintegration of bark particles was observed during mechanical agitation. This caused problems with filtration and subsequent metal analysis. Although organics leaching can be stabilised by pre-treatments of formaldehyde and nitric acid, this
adds additional costs, incurs the use of harmful undesirable reagents and the generation of additional wastes (Gloaguen and Morvan, 1997).

*Fucus vesiculosus* was the least efficient material under the conditions tested. However, the removal was fast; >80.1 % over the first 20 minutes. Although, the efficiency increased as initial Cu(II) concentration increased, equilibrium uptake was not achieved (Figure 4.3). Similar trends were reported by Stirk and van Staden (2000), Williams and Edyvean (1997) and Senthilkumar *et al.* (2006) using brown seaweeds and their derivatives. A kinetic modelling study by Schiewer and Volesky (1995) concluded the rapid uptake of metals by seaweed occurs via ion-exchange with protons from mildly acidic functional groups followed by a slow diffusion of metals into cell structures. For the interested reader a detailed review describing the complex biochemistry involved with the uptake of metals by brown seaweeds was reported by Davis *et al.*, (2003).

Potential disadvantages of using seaweed were the disintegration of particles during mechanical agitation, swelling on contact with water and leaching of soluble alginates. This resulted in difficulties with filtration of samples and interference effects with metal analysis. Also, small scale column studies (results not shown) demonstrated that it was not practical to use seaweed due to clogging and increasing back pressures which resulted in the delivery pipes blowing off. Similar hydrodynamic flow restrictions and pressure differentials were reported by Stirk and Van Staden (2000, 2004) using brown seaweeds. Although this can be overcome by immobilising the seaweed particles in a stable matrix (e.g. alginate bead forms), this involves time consuming pre-treatments and expensive reagents (Tan *et al.*, 2002; Papageorgio *et al.*, 2006).
4.4. CONCLUSIONS

CMC, MMC, brown seaweed (*Fucus vesiculosus*) and Douglas fir wood bark (*Pseudotsuga menziesii*) were evaluated as biosorbents for the removal of Cu(II) from aqueous solutions. A number of conclusions were made and are summarised below:

1. All materials showed some potential as biosorbents. Cu(II) removal by wood bark was rapid and efficient at low concentrations but decreased abruptly as concentration increases. Particle disintegration, leaching of organics caused discoloration of water, difficulties with filtration and metal analysis.

2. *Fucus vesiculosus* was inefficient at low Cu(II) concentrations, but removal improved as concentration increases. Equilibrium uptake was not attained and this merits further investigation. Degradation of particles during agitation and leaching of soluble alginates caused problems with filtration and metal analysis. Swelling of particles prevented effective use for columns studies.

3. Cu(II) removal by CMC and MMC was fast and efficient over the 100-1000 mg/L range and particles were resistant to abrasion during mechanical agitation. Therefore, CMC and MMC were considered to offer the best potential for development as biosorbents. This hypothesis will be tested further in Chapters 5 and 6 by inter-comparison studies with commercial sorbents.

Although MMC was less efficient than CMC in some studies, MMC is less labour intensive and cost effective to produce from the raw material. Therefore, MMC was selected for further screening to establish the biosorption potential for a range metals. The results of these studies are presented in Part B.
4.5. METALS COMPARISON (PART B)

4.5.1 Introduction

Although many biomaterials bind metals effectively (Bailey et al., 1999), only those with a high uptake capacity and selectivity are suitable for development in larger scale biosorption columns (Kratochvil et al., 1998; Volesky, 2003). Another desirable feature of biosorbents is the ability to remove metals effectively from dilute concentrations (e.g. 0.5-20 mg/L). Strict new water quality legislation has reduced the Maximum Contaminant Limits (MCLs) for metals discharged into receiving waters from industrial effluents (Water Framework amended Directives 80/68/EC and 2000/60/EC).

Conventional treatments for metal removal at low concentrations include solvent extraction, electro-deposition, membrane separation processes and ion-exchange resins (Tels, 1987; Grimm et al., 1998). However, these processes can be expensive due to high energy inputs, chemical requirements or ineffective because of organic fouling (see Chapter 1 Table 1.14). Therefore, there is an urgent need for low cost alternatives to compete with or complement existing treatment options.

Based on conclusions from Part (A), this section extends the evaluation of MMC as a biosorbent for the removal of environmentally relevant metals. Laboratory scale column studies were conducted to assess the applicability and selectivity for K(I), Li(I), Ca(II), Mg(II), Cd(II), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II). In addition, batch studies were conducted to assess the effects of contact time, metal concentration (1-1000 mg/L) and particle size (<250, 250-800, 800-2000 and > 2000 µm) on removal efficiency and uptake of Cu(II), Hg(II), Pb(II) and Zn(II) from single metal solutions.
4.5.2 Column Studies (selectivity of metals)

Bench scale column studies were performed to determine the selectivity / affinity of MMC for a range metals. The results are shown in (Figure 4.4 a, b and c).

Figure 4.4: Removal of metals by MMC. (a) alkali and alkaline earth metals, (b) transition metals and (c) toxic heavy metals. All metal solutions 500 mg/L, flow rate 6.4 ml/minute, pH = 4.5, T = 20º C ± 2º C, 20 g MMC, 250-800 µm particle size.
MMC shows a low affinity for the alkali metals Li(I) and K(I) with maximum removal efficiencies of 19.1 % and 35.0 % respectively (Figure 4.4 a). While there was a high initial removal of the alkaline metals Ca(II) and Mg(II), 90.0 % and 74.0 % respectively, this decreased abruptly after 50 mg was delivered to the column. Considerably higher removals were observed for the transition metals, Cu(II), Ni(II) and Zn(II) with 99.0, 98.1 and 99.6 % respectively (Figure 4.4 b). While removals of the heavy metals Pb(II), Hg(II) and Cd(II) were highly efficient with 99.3, 98.4 and 97.8 % respectively (Figure 4.4 c).

These results support the findings of Muzzarelli (1977), Muzzarelli et al. (1989) and An et al. (2001) who reported the effectiveness of chitinous materials for the uptake of transition and heavy metals from aqueous solutions. Crab carapace and its derivatives chitin and chitosan selectively bind virtually all group III transition metals, but show a poor affinity for the group I and II alkali and alkaline earth metals.

According to the Pearson hardness scale, metals can be divided into two classes, A and B depending on whether they form stable complexes with ligands (Pearson, 1963). This classification of metals was further refined by Nieboer and McBryde (1973) and Nieboer and Richardson (1980) to A, B and borderline metals based on atomic properties, solution chemistry and the preference of metals to form ionic or covalent bonds. These researchers proposed that Class A (or hard metals) show a preference to form ionic bonds with oxygen containing ligands (e.g. OH\(^-\), HPO\(_3\)^{2-}, CO\(_3\)^{2-}, R-COO\(^-\)). While class B (or soft metals), form strong covalent bonds with ligands containing nitrogen and sulphur (e.g. CN\(^-\), R-S\(^-\), S-H, NH\(_2\)^-). While there is a clear distinction between class A and B metals, borderline metals form an intermediate class and have a strong affinity for ligands containing sulphur, nitrogen and oxygen donor atoms.
Figure 4.5 shows the class of the metals used for these studies based on the Nieboer and Richardson (1980) classification system. Where metal interactions with ligands are determined by three parameters: the metal ion charge ($Z$), the radius ($r$) and the electronegativity ($X_m$). The factor $(Z^2/r)$ can be considered as an indicator of ion charge density and is related to electrostatic binding strength, while $(X_m^2 r)$ represents the valence orbital energy and is a measure of the strength of covalent bonding relative to ionic bonding. The electro-potential and lower covalent index values of Li(I), K(I), Ca(II), Mg(II) with respect to the other metals (Figure 4.5) may explain the low uptakes observed for these metals (Nieboer and Richardson, 1980; Brady and Tobin, 1995).

This study demonstrated the applicability of MMC for use in columns and the affinity of MMC for Cd(II), Cu(II), Hg(II), Ni(II), Pb(II), Zn(II) at laboratory scale concentrations. This prompted the need for more detailed investigations to determine the biosorption potential of MMC over a wider concentration range. Therefore, a series of batch studies were designed to evaluate the effects of contact time (0-60 minutes), concentration (1-1000 mg/L) and particle size (<250, 250-800, 800-2000 and >2000 µm) on the removal of Cu(II), Hg(II), Pb(II) and Zn(II) from single metal solutions.
4.5.3 Detailed investigations

4.5.3.1 Effects of Contact time

MMC was evaluated for the removal of Cu(II), Hg(II), Pb(II) and Zn(II) from single metal solutions. Figure 4.6a and b shows the metal uptake and removal efficiencies as a function of contact time at initial metal concentrations of 100 mg/L and 500 mg/L respectively.

![Figure 4.6: The effects of contact time on the removal of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC. Graph (a) C₁ = 100 mg/L. Graph (b) C₁ = 500 mg/L. All studies pH₁ = 4.5, V = 100 ml, T = 20 °C ± 2 °C, 5 grams MMC, 250–800 µm particle size.](image-url)
At metal concentrations of 100 mg/L, initial uptake of Pb(II), Hg(II) and Cu(II) was rapid and efficient removing 1.99 mg/g (99.8%), 1.88 mg/g (93.6%), and 1.68 mg/g (84.4%) respectively after 5 minutes (Figure 4.6 a). Thereafter, uptake was gradual and pseudo-equilibriums were reached within 40 minutes. These results confirm the Cu(II) sorption kinetics found in Part A (section 4.3.1.1). The initial uptake of Zn(II) was more gradual and increased steadily over time reaching a maximum of 1.78 mg/g (88.6%) at 60 minutes (Figure 4.6 a). The maximum uptakes of Pb(II), Hg(II) and Cu(II) by MMC were 2.0 mg/g (99.9%), 1.9 mg/g (96.4%) and 1.3 mg/g (96.1%) mg/g at contact times of 40, 20 and 60 minutes respectively.

In summary, the order of maximum metal uptake by MMC at 100 mg/L was Pb(II) >Hg(II)>Cu(II)>Zn(II).

At a metal concentration of 500 mg/L, initial uptake of Cu(II) and Pb(II) by MMC was also fast and efficient removing 9.9 mg/g (99.2%) and 9.8 mg/g (98.6%) mg/g respectively after 20 minutes (Figure 4.6 b). While the initial uptake of Hg(II) and Zn(II) was rapid over the first 20 minutes, with 6.9 mg/g (69.4%) and 5.1 mg/g (51.6%) respectively. Thereafter, removal of Hg(II) increased slowly and did not reach equilibrium (Figure 4.6 b). The maximum uptakes were 9.9 mg/g (99.3%), 9.9 mg/g (99.3%), 8.0 mg/g (80.3%) and 5.2 mg/g (52%) at contact times of 40, 40, 60 and 60 minutes for Cu(II), Pb(II), Hg(II) and Zn(II) respectively.

In summary, the order of maximum metal uptakes by MMC at 500 mg/L was Cu(II)≥Pb(II)>Hg(II)>Zn(II).
4.5.3.2 Effects of metal concentration

Figure 4.7 show the percentage removal of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC as the initial concentrations were increased from 1 to 1000 mg/L.

![Figure 4.7: The effects of initial concentration on the removal of Cu(II), Hg(II), Pb(II) and Zn(II). All studies 60 minutes contact time, pH = 4.5, V = 100 ml, T = 20 °C ± 2 °C, 5 grams MMC, 250–800 µm particle size](image)

The removal of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC was highly efficient up to a concentration of 50 mg/L with removals of 99.5, 98.6, 98.3 and 91.8 % respectively (Figure 4.7). While Pb(II) removal remained fairly constant over the entire concentration range, 98.1 % up to 1000 mg/L. The removal of Cu(II) and Hg(II) gradually decreased to 78.0 % at 500 mg/L then decreased rapidly to 53.0 and 15.7 % respectively at 1000 mg/L. The removal of Zn(II) decreases steadily as concentration increased above 100 mg/L to 37.2 % at 1000 mg/L.

In summary, the order of highest removal efficiencies by MMC as concentration increases from 1 to 1000 mg/L was Pb(II)>Hg(II)>Cu(II)>Zn(II).
The transition metals Cu(II) and Zn(II) and highly toxic metals Hg(II) and Pb(II) show a strong affinity for MMC and can be removed effectively (>99.0 %) at concentrations ranging from 1-50 mg/L. This is particularly evident for Hg(II) with ~100 % removal (or below the FAAS limits of detection) up to a concentration of 10 mg/L (Figure 4.7). This is a very desirable feature of biosorbent materials and may provide the potential for bioremediation applications for a variety of industrial effluents.

In summary, the order of removal efficiency by MMC at initial concentrations ranging from 1-50 mg/L was Hg(II) > Cu(II) > Pb(II) > Zn(II)

It is also interesting to note, that in general, the metal removals appear to correlate directly with the class of metal and the covalent index values (Figure 4.5). As the MMC has mixed functionality (see Chapter 3 Table 3.4), and includes hydrogen, oxygen, nitrogen and sulphur functional groups (ADAS UK Report, 2006). The effective uptake of transition and heavy metals observed in these studies may be accounted for by strong covalent bonding to available metal binding ligands containing these donor atoms.
4.5.3.3 Effect of Particle size

Figure 4.8a, b and c show the percentage removal of Cu(II), Hg(II) and Pb(II) from single solutions for various MMC particle sizes at an initial concentration of 500 mg/L.

Figure 4.8: The effects of particle size on the removal of Cu(II) (a), Hg(II) (b) and (c) Pb(II). Contact time 60 minutes, C_0 500 mg/L, pH_1 4.5 and no control for Hg(II) and Pb(II) and pH_1 4.5 and regulated to 4.3-4.7 for Cu(II), T = 20 °C ± 2 °C, V = 100 ml, 5 grams MMC, agitation rate 350 rpm. These studies were not conducted for Zn(II).
In general, as particle size decreases, there was a corresponding increase in metal removal due to an increase in surface area and metal binding sites (Figure 4.8). Under the conditions investigated, MMC removed 89.0% Cu(II) with the <250µm particle, steadily decreasing to 11.5% with the >2000µm size fraction (Figure 4.8 a). A similar removal was observed for Hg(II) with 83.4% with <250µm decreasing to 14.1% for >2000µm (Figure 4.8 b). However, this was not observed for Pb(II) and high removal efficiencies were obtained (81.6 to 98.7%) for all particle sizes (Figure 4.8 c). This indicates that surface area is not a significant factor for the effective uptake of Pb(II).

4.5.4 Discussion

The rapid uptake of Cu(II), Hg(II) and Pb(II) shows the affinity of MMC for these metals (Figure 4.6 a and b). Similar Cu(II) and Pb(II) sorption kinetics were reported by (Sheng et al., 2004) using algal biomass and were attributed to the heterogeneous functionality. While Low and Liew (2000) and Gerente et al. (2000) reported similar uptakes of Pb(II) using biosorbents derived from spent grain and sugar beet pulp. Although the removal of Hg(II) by MMC was highly efficient at low concentrations, this decreased abruptly at higher concentrations. Therefore, effective removal of Hg(II) appears to be concentration dependant and saturation of available binding sites occur at higher concentrations.

The uptake of Zn(II) by MMC was the lowest of the transition metals for all contact times and concentrations. This is in accordance with the literature, where in general, most biosorbents showed a lower uptake of Zn(II) than Cu(II), Hg(II) and Pb(II). For example, Bakkaloglu et al., (1998) and Iqbal and Edyvean, (2004) reported a poor removal of Zn(II) by seaweeds and fungal biomass compared to other metals.
At concentrations ranging from (1-1000 mg/L), removal of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC were generally efficient, particularly for Pb(II) which remained consistently >98.0%. This shows the strong affinity of MMC for heavy metals and offers potential for a range of applications. The order of metal uptake appears to be highly dependant on initial concentration, and metal type (Table 4.5). Similar orders of metal removal were found by An et al., (2001) using crab carapace and Iqubal and Edyvan, (2004) using seaweed.

At low concentrations (1–50 mg/L), removal of all metals was rapid and highly efficient and the final concentrations were in compliance with the current discharge limits (see Chapter 1 Table 1.12). This offers potential for MMC to be used as a polishing stage or to compliment existing treatments that are ineffective at low concentrations.

Findon et al. (1986) reported similar results with small variations in Cu(II) removal as chitosan particle size was decreased from 1000 µm to 210 µm. However, these authors suggested that the number and distribution of amine functional groups were more significant than surface area. This removal trend was also observed by Vijayaraghavan et al. (2005a) using crab shells. The relationship between smaller particle sizes and increased metal removal has also been observed for other natural materials e.g. wood products (Gloaguen and Morvan, 1997) and peat (McKay et al., 1999).

The increase in metal removal with decreasing particle size suggests that metals are being preferentially adsorbed onto specific surface binding sites and do not fully penetrate into the particles. Similar results were reported by Evans et al., (2002) using a chitosan based crab carapace for the removal of Cd(II). These authors suggested that intra-particle diffusion was the sorption rate limiting step. This hypothesis will be tested for MMC in
Chapters 5 and 7 using SEM-EDAX micro analysis and an Intra-particle diffusion kinetic model.

4.6. GENERAL CONCLUSIONS

MMC, CMC, *Fucus vesiculosus* and Douglas fir wood bark were screened as biosorbents for the removal of metals from aqueous solutions. A number of conclusions were drawn and these are summarised below.

1. The removal of Cu(II) was fast for all materials with >95.0 % of the eventual total taking place in the first 5 to 20 minutes, while contact times longer than 60 minutes showed no improvement.

2. MMC and CMC were highly efficient (up to 99.0%) over the 100-1000 mg/L range. Wood bark was efficient at low concentrations, 93.0 % at 100–200 mg/L. While *Fucus vesiculosus* was less efficient (46.8%) at low concentrations 100-200 mg/L, but the efficiency improved as concentration increased.

3. Wood bark and *Fucus vesiculosus* disintegrated during mechanical agitation, leached tannins and alginates causing filtration and metal analysis problems. Swelling of *Fucus vesiculosus* restricted its use in columns. CMC and MMC particles were stable during mechanical agitation and in acidic solutions.

4. The applicability of MMC for use in columns was established and the metal affinities followed the order: Li<K<Mg<Ca>Zn<Ni<Cu<Cd>Hg<Pb

5. Extended batch studies showed that the removal of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC was fast and efficient over a large concentration range 1-1000 mg/L
6. In general, as particle size decreases there was a corresponding increase in metal removal due to the increase in surface area and metal binding sites.

This screening study, demonstrated that CMC, MMC, *Fucus vesiculosus* and Douglas fir wood bark (*Pseudolsuga menziessii*) all showed potential for the removal of Cu(II) from single metal solutions. However, CMC and MMC derived from crab carapace were more robust under mechanical agitation and showed significantly less swelling. Extended studies confirmed the potential of MMC for use in column studies and the rapid uptake and retention of Cu(II), Hg(II), Pb(II) and Zn(II) over a wide concentration range and one representative of industrial wastewater. Biosorption processes that proceed in less than one hour are likely to be favoured by the engineering community, as the kinetics of metal removal directly effect the volume of effluent that can be treated.

Crab carapace is a waste material that is readily available locally and easy to prepare into durable granular forms. Therefore, the evaluation of MMC and CMC as metal biosorbents will be extended further in Chapter 5 by and inter-comparison with commercial chitin flakes (derived from the *Cancer pagurus*) and crab chitosan flakes produced in our laboratory from commercial chitin.
5. CHAPTER 5 INTER-COMPARISON OF CHITINOUS MATERIALS
In Chapter 4, shellfish wastes MMC and CMC, brown seaweed (*Fucus vesiculosus*) and Douglas fir wood bark (*Pseudolsuga menziessii*) were screened as biosorbents for the removal of Cu(II) from aqueous solutions. While seaweed and wood bark showed potential, MMC and CMC were more durable to mechanical agitation and efficient over the 100-1000 mg/L range. Extended studies showed that MMC was also effective for the removal of Cu(II), Hg(II), Pb(II) and Zn(II) over the 1-1000 mg/L range and applicable for use in laboratory scale column studies. This Chapter develops the assessment of MMC and CMC as biosorbents by an inter-comparison with biopolymers chitin and chitosan (derived from *Cancer pagurus*) for the removal of Cu(II) from single metal solutions.

5.1. INTRODUCTION

Chitin and chitosan are important biopolymers in water treatment processes due to their low toxicity, biodegradability, biocompatibility and selectivity for metals (Muzzarelli, 1973 and 1977; Stankiewicz *et al*., 1998; Domard *et al*., 1996; Guibal, 2004; Crini, 2005). After cellulose, chitin is the most abundant natural polymer found on Earth with the main commercial sources coming from crustacean shells (Leffer, 1997). The chitin is extracted from crustaceans by acid and alkaline treatments to remove calcium carbonate, oils and proteins (Pradhan *et al*., 2005). Chitosan is a derivative of chitin and produced by the alkaline deacetylation of chitin, (No *et al*., 1998).

A simplified schematic showing the extraction processes and the production of chitin and chitosan from the carapace of the edible crab (*Cancer pagurus*) is presented in Figure 5.1
Chitosan is soluble in most mineral and organic acids and the protonation of amino groups results in the electrostatic repulsion of metal cations (Delben et al., 1989; Guibal et al., 1994). This can reduce the metal removal efficiency of chitosan in acidic effluents and limits the potential for metal recovery and material regeneration (Crini, 2005). Although cross-linking by glutaraldehyde or carboxymethyl can improve the structural stability in acidic solutions, this reduces sorption efficiency and restricts access to metal binding amine groups (Guibal et al., 1995; Varma et al., 2004). Recent studies with low cost biosorbents derived from crustacean shells have proven to be effective for the removal of metals from acidic solutions (Nui and Volesky, 2001, 2003; Rae and Gibb, 2003).
Based on the structural stability and metal removal efficiencies achieved by MMC and CMC in Chapter 4, the objective of this Chapter was to compare MMC and CMC with commercial chitin flakes (derived from *Cancer pagurus*) and crab chitosan produced from chitin for the removal of Cu(II) from single metal solutions. The removal efficiencies and specific uptakes by the chitinous materials was determined with batch adsorption studies designed to test the effects of contact time, concentration, solution pH, particle size and mass loading.

5.2. MATERIALS AND METHODS

- MMC and CMC

The collection and preparation of MMC and CMC was described in Chapter 2 (sections 2.2.1 and 2.2.2). MMC was used with the <250, 250-800, 800-2000 and >2000 µm particle sizes and CMC at the 250-800 µm size.

According to Roer and Dillaman (1984), crustacean carapace is comprised of four distinct layers (Figure 5.2).

![SEM micrograph showing the cuticle layers of the crustacean carapace. (Adapted from Roer and Dillaman (1984) with permission)](image)

**Figure 5.2:** SEM micrograph showing the cuticle layers of the crustacean carapace. (Adapted from Roer and Dillaman (1984) with permission)
The epicuticle is the thinnest layer and contains lipoproteins impregnated with calcium salts, while the exocuticle and endocuticle are enriched with chitin and protein fibres (Hegdahl, 1977 a, b and c and Figure 3.2b). The endocuticle is the thickest and most heavily calcified layer and can contain up to 73% of chitin by weight (Welinder, 1975). The membranous layer consists of chitin and protein, with chitin representing ~74% of the organic material. Figure 5.3 shows a simple illustration of the cuticle layers.

![Diagram of crustacean carapace cuticular layers](image)

**Figure 5.3:** Composition of crustacean carapace cuticular layers. MM = Mineral matrix containing proteins with affinity to calcium ions, CaCO₃ = CaCO₃ crystals and protein anchors from the MM layers. CP = Carrier proteins containing chitoprotein complexes with no affinity to calcium ions. (Adapted from Stumm and Hesse, 2001 with permission)

- **Chitin and chitosan**

Chitin flakes (derived from *Cancer pagurus*) were obtained from Aldrich, U.K. The flakes were crudely milled to provide <250, 250-800, 800-2000 and >2000 µm particle sizes.

Chitin is a high molecular weight linear polysaccharide characterised by repeating monomers of β-(1→4)-linked N-acetyl-D-glucosamine (Muzzarelli, 1977). The molecular structures of chitin, chitosan and cellulose are similar, but with chitin many of the hydroxyl groups at the C-2 position are replaced by N-acetyl groups (Figure 5.4).
With chitosan, the N-acetyl groups of chitin are converted into amine groups by thermo alkaline deacetylation. However, in acidic solutions (e.g. pH<4), chitosan becomes a linear polyelectrolyte with a high surface charge density, with one positive charge per glucoseamine unit (Figure 5.4 middle). This can result in the electrostatic repulsion of metal cations.

**Figure 5.4:** Molecular structures of chitin, chitosan and cellulose. Boxes show the monomers N-acetylglucoseamine (GlcNAc), glucoseamine (GlcN), and glucose (Glc) respectively. (Adapted from Sturm and Hesse, (2000) with permission)

For these studies, chitosan flakes with approximately 87 % degree of deacetylation were produced from the commercial chitin flakes following the economical procedure proposed by Aluminar and Zainuddin (1996). Refer to Chapter 2 section 2.2.4 for a brief summary of the method. The deacetylated product was mechanically milled and graded to provide <250, 250-800, 800-2000 and >2000 µm particle sizes.
Alkaline deacetylation of the chitin flakes leads to the expansion of the micro-pore structures, a slight increase in BET surface area and exposure of additional amino groups (Figure 5.5 and Table 5.1). The amino groups of chitosan are highly reactive and bind many of the transition and heavy metal ions via electrostatic interactions and covalent bonding with donor electron pairs in nitrogen atoms (Marsi et al., 1974; Muzzarelli, 1973; Dambies et al., 2001; Varma et al., 2004).

![Figure 5.5: SEM micrographs showing chitin flakes (a) and (b) deacetylated chitin (chitosan flakes).](image)

To produce 1 kg of chitosan from chitin it requires 2.5 kg of sodium hydroxide and produces large volumes of toxic liquid wastes which have to be disposed of, consequently, this significantly increases the cost of this biopolymer (Table 5.1).

### Table 5.1: Selected characteristics of chitinous materials (250-800 μm particle size).

<table>
<thead>
<tr>
<th>Material</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>Surface area (m²/g)</th>
<th>Cost (£/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMC</td>
<td>15.1</td>
<td>1.7</td>
<td>1.1</td>
<td>22.5</td>
<td>1.2</td>
</tr>
<tr>
<td>CMC</td>
<td>11.4</td>
<td>1.5</td>
<td>1.2</td>
<td>33.4</td>
<td>8.0^a</td>
</tr>
<tr>
<td>chitin</td>
<td>46.6</td>
<td>6.7</td>
<td>4.4</td>
<td>3.9</td>
<td>6.0^b</td>
</tr>
<tr>
<td>chitosan</td>
<td>32.4</td>
<td>5.1</td>
<td>6.0</td>
<td>6.0</td>
<td>85.0^a</td>
</tr>
</tbody>
</table>

**Notes:** ^a Estimated values made in 2003, ^b Aldrich Catalogue price 2003
• **Material characterisation**

SEM-EDAX analysis was used to examine the surface microstructures and show the distribution of copper in raw materials and those contacted with Cu(II) solutions. The BET specific surface areas and the C, H and N contents of each material were determined using the methods described previously see Chapter 2 (sections 2.3.3, 2.3.6 and 2.3.7).

• **Batch adsorption studies**

The batch adsorption studies were conducted at room temperature (21 °C ± 2 °C) by agitating (350 rpm) weighed quantities of materials in 100 mL of Cu(II) solutions at the required contact time, initial concentration, pH and particle size. All studies were conducted in triplicate and the means presented. If the standard deviations are greater than 10 % these are shown as error bars on graphs or included in the text or tables.

• **Metal solutions and chemical analysis**

Stock Cu(II) solutions were prepared by dissolving analytical grade anhydrous copper sulphate CuSO₄ (Aldrich U.K) in ultra pure water (Millipore Direct 3 system). Copper sulphate was chosen as sulphate ions are generally present as background ions in most surface waters and industrial wastewater effluents (Stumm and Morgan, 1996). The initial and residual concentrations of Cu(II) before and after contact with materials were determined using an Atomic Absorption Spectrometry (AAS) using the instrumental parameters described in Chapter 2 (see sections 2.4.6 and 2.4.9).
• **Control of pH**

As carapace from the *Cancer pagurus* contains up to 50% CaCO$_3$ (Welinder, 1975), there is a tendency for the dissolution of CaCO$_3$ during agitation with aqueous solutions. This can result in an abrupt increase in solution pH (Figure 5.6b) and at pH >5 the formation of insoluble Cu(II) precipitates (Figures 5.6a) for example, CuCO$_3$(s) or Cu(OH)$_2$(s) (Stumm and Morgan, 1992).

![Figure 5.6: The effects of pH: (a) the onset of Cu(II) precipitation as the initial solution pH (pH$_i$) is increased from 1 to 7, 60 minutes shaking time, 350 rpm, initial Cu(II) concentration 500 mg/L (with no MMC or CMC) and (b) evolution of pH with 5 grams of MMC and CMC in ultra-pure water with no Cu(II) in solution. Both studies were conducted at room temperature (20 °C ± 2.0 °C).](image)

Therefore, in these studies, batch experiments were conducted with no pH control and the pH controlled to assess for the relative contributions of sorption and precipitation processes to the overall Cu(II) removal. Under controlled conditions, the solution pH was monitored at regular intervals and regulated to 4.3-4.7 by the drop-wise addition of 0.1 M HCl or 0.1 M NaOH (e.g. a pH at which Cu precipitation is not thermodynamically favoured).
5.3. RESULTS AND DISCUSSION

5.3.1 Effects of pH on chitosan structure

During studies with the pH controlled to 4.3-4.7 it was noted that the chitosan particles were transformed into a gelatinous substance. Therefore, SEM micrographs were taken and used to examine the micro-structures of particles exposed to these acidic solutions (Figure 5.7).

![Figure 5.7](image)

**Figure 5.7**: SEM micrographs of chitosan (250-800 µm particle size), (a) raw chitosan flakes, (b) chitosan agitated with 500 mg/L Cu(II) at room temperature for 60 minutes, pHᵢ = 4.5 and no control the final pH was 8.7 and (c) chitosan contacted with 500 mg/L Cu(II) pHᵢ = 4.5 and pH controlled to 4.3-4.7.

The images clearly show a change in the micro-structure when exposed to acidic solutions (Figure 5.7c). The surface appears to be flattened and the open pore structure has collapsed with respect to raw chitosan and particles exposed to solutions with no pH control (Figure 5.7a and b). The change in surface morphology was attributed to the partial dissolution of chitosan in these acidic solutions. This structural collapse would affect the sorption of Cu(II) due to restricted accessibility to intra-particle binding sites. Muzzarelli *et al.* (1989) reported similar structural degradation and reduced metal uptake using chitosan in the same pH range. Therefore, apart from some preliminary studies already conducted with chitosan all others were done with no pH control.
5.3.2 Effects of contact time and pH

Previous biosorption studies with chitin containing materials revealed that the effective uptake of metals was dependant on the pH (Fourest and Roux, 1992; Guibal et al., 1994; Veglio et al., 2001). Therefore, experiments with MMC, CMC, chitin and some studies with chitosan were performed with and without pH control to assess the affects on Cu(II) removal. Figure 5.8 shows the percentage removals at an initial concentration of 500 mg/L. The data for MMC and CMC (no pH control) was presented in Chapter 4 and are used here for comparison.

![Figure 5.8: Effects of contact time and pH on Cu(II) removal by MMC, CMC, chitin and chitosan, (a) C₁ 500 mg/L, pH₁ 4.5 and no control, (b) C₁ 500 mg/L, pH₁ 4.5 and controlled to 4.3-4.7, V = 100 ml, T = 20 ºC ± 2.0 ºC, 5 grams, 250-800 µm particle size. Values in legend brackets are the final pH (pHᵢ) at 60 minutes.](image-url)
With no pH control, removal of Cu(II) by chitin and chitosan show a similar trend to that observed for MMC and CMC in Chapter 4 (see Fig 4.2). There was a rapid removal over the first 20 minutes with 33.7 and 93.7 % for chitin and chitosan respectively followed by a slow approach towards equilibrium (Figure 5.8 a). Contact times longer than 60 minutes showed no improvement in removal. The highest removal efficiencies were 99.3, 98.6, 37.1 and 95.4% at 40 minutes for MMC, CMC, chitin and chitosan respectively (Figure 5.8 a). This corresponds to uptakes of 9.9, 9.8, 3.7 and 9.5 mg/g for MMC, CMC, chitin and chitosan respectively.

In summary, order of efficiencies with no pH control were MMC>CMC>chitosan>chitin

With pH controlled to 4.3-4.7, the highest removals were 78.7, 81.2, 35.6 and 74.5% at 60, 40, 60 and 60 minutes for MMC, CMC, chitin and chitosan respectively (Figure 5.8 b). This corresponds to Cu(II) uptakes of 7.8, 8.1, 3.5 and 7.4 mg/g.

In summary, order of efficiencies with pH controlled were CMC>MMC>chitosan>chitin.

In effect, with pH controlled, the removal of Cu(II) decreased by approximately 20.0% for MMC, CMC and chitosan and 2.0% for chitin. This decrease was attributed to the lack of precipitation at pH >5. In addition, at this pH range, the protonation of amine functional groups on chitosan would result in electrostatic repulsion (see Figure 5.4). Furthermore, SEM analysis of chitosan particles exposed to these acidic conditions revealed degradation of porous structure (Figure 5.7c) which would restrict accessibility of Cu$^{2+}$ to intra-particle binding sites. Similar observations were reported by Guibal et al. (1999) and Chui et al. (1996) using crab chitin and chitosan for the removal of Cu(II).
5.3.2.1 Evolution of pH

If temperature is held constant, pH is the principal parameter affecting the removal of metals in biosorption studies (Volesky, 1990; Fourest and Roux, 1992; Pagnanelli et al., 2003). Therefore, pH was monitored during Cu(II) sorption by MMC, CMC, chitin and chitosan. Figure 5.9 shows evolution of pH at a Cu(II) concentration of 500 mg/L.

![Figure 5.9: Evolution of pH with MMC, CMC, chitin and chitosan immersion over time, pH_i = 4.5, V = 100 ml, T = 20 °C ± 2.0 °C, 5 grams, 250-800 µm particle size. Values in legend are pH_f at 60 minutes.](image)

The pH increased rapidly on contact with MMC, CMC and chitosan from 4.5 to 6.9, 8.5 and 8.5 respectively after 10 minutes (Figure 5.9). The increase in pH can be explained by dissolution of CaCO₃ from MMC and CMC and residual NaOH on chitosan from the deacetylation process and would result in Cu(II) precipitation (see Figure 5.6a). The increase in pH was less pronounced for chitin as most of the CaCO₃ is removed by HCl during extraction from carapace (see Figure 5.1 and Rhazi et al., 2000). The alkaline properties of MMC and CMC and the Cu(II) removals obtained in these studies may offer potential for the neutralisation and detoxification of highly acidic Cu(II) bearing effluents.
The results from these studies are consistent with those reported by Muzzarelli (1989) and Delben et al. (1989) using chitin, chitosan and cross-linked derivatives for Cu(II) removal from aqueous solutions. These authors attributed the more effective removal of Cu(II) by chitosan compared to chitin to the more reactive amine groups on chitosan (see Figure 5.4). This concurs with an earlier study by Eiden et al. (1980) who proposed that the higher numbers of accessible amino groups on chitosan are more effective for binding Cu(II) than the acetyl groups in chitin. This would account for the lower Cu(II) removal by chitin observed in this study.

It was concluded from these studies that a contact time of 60 minutes was sufficient for most of the Cu(II) removal to have taken place and used for subsequent studies. With no pH control, sorption and precipitation mechanisms accounted for approximately 80.0 and 20.0% respectively of the total Cu(II) removal by MMC, CMC and chitosan. Solution pH had a small affect on the removal efficiency (~ 2.0%) and uptake of Cu(II) by chitin. However, the structural and chemical stability of chitosan was affected in acidic solutions (pH < 4.7) due to partial dissolution and protonation of amine groups. Therefore, all subsequent studies with chitosan were conducted with no pH control.

Commercial chitin was the least efficient material (~ 37.0%) with or without pH control. While MMC and CMC were highly efficient with or without pH control (~79.0 – 99.0%) and compared favourably with chitosan. The effective removal of Cu(II) by MMC and CMC was attributed to larger surface areas, mixed functionality and macro and micro porosity (see Table 5.1 and Figure 3.1). In addition, the basic nature of MMC and CMC provides a buffering capacity at low pH preserving the structural and chemical stability. The change in orders of removal by MMC and CMC with pH control was attributed to dissolution of more CaCO₃ with the crude milling process and no ultrasonic cleaning.
5.3.3 Effects of concentration (no pH control)

Figure 5.10 shows (a) percentage Cu(II) removal and (b) specific uptake (q), by MMC, CMC, chitin and chitosan for the 100-1000 mg/L range. Data for MMC and CMC (% removal no pH control) was presented in Chapter 4 and are used here for comparison.

**Figure 5.10:** The effects of Cu(II) concentration (a) percentage removal and (b) specific uptake q (mg/g). All studies 60 minutes contact time, pH_i = 4.5 and no pH control, V = 100ml, T = 20 °C ± 2.0 °C, 5 grams, 250–800 µm particle size. Values in legend are pH_i at 60 minutes.
As shown in Chapter 4, the removal of Cu(II) by MMC and CMC with no pH control was highly efficient removing 85.1-99.0 % over the 100-1000 mg/L range (see Figure 4.3). In this Chapter, chitosan was more efficient than MMC and CMC at lower concentrations removing >95.0 % up to 500 mg/L then decreased slightly to 92.1 % at 1000 mg/L (Figure 5.10a). Commercial chitin removed 93.8 % at 100 mg/L then the efficiency decreased rapidly to 13.5 % at 1000 mg/L. The highest efficiencies achieved were 96.5, 98.7, 93.8 and 98.4 % for MMC, CMC, chitin and chitosan respectively at concentrations of 200, 1000, 100 and 200 mg/L (Figure 5.10a). While the highest Cu(II) uptakes were 16.9, 19.7, 4.4 and 18.5 mg/g for MMC, CMC, chitin and chitosan respectively at concentrations of 1000, 1000, 500 and 1000 mg/L (Figure 5.10b).

In summary, the order of removal efficiencies and specific uptakes of Cu(II) with no pH control were CMC> chitosan>MMC>chitin

It is also interesting to note that the uptake (mg/g) of Cu(II) by MMC, CMC and chitosan appears to be directly proportional to the initial concentration over the 100-1000 mg/L range (Figure 5.10b). While this trend was only observed for chitin up to a concentration of 500 mg/L, thereafter the uptake decreased steadily. This suggests that the metal binding sites were being filled (Figure 5.10b). It was also observed that the equilibrium uptakes were not attained for MMC, CMC and chitosan at a concentration of 1000 mg/L (Figure 5.10b).

Therefore, extended concentrations studies (up to 4000 mg/L) were conducted to try and establish the Cu(II) uptake capacities of MMC and CMC at equilibrium conditions. The results from these studies are shown in (Figure 5.11).
Figure 5.11: Extended concentration study with MMC and CMC. All studies 60 minutes contact time, pH$_i$ = 4.5 and no pH control, V = 100 ml, T = 20 °C ± 2 °C, 5 grams, 250–800 µm particle size. These studies were not conducted for chitin or chitosan.

When the initial concentration was increased, the Cu(II) uptake by MMC and CMC continued to increase and equilibrium uptakes of 30 and 35 mg/g were reached at 2000 and 3000 mg/L for CMC and MMC respectively (Figure 5.11). Thereafter, the uptake decreased gradually to 25.2 and 33.1 mg/g at 4000 mg/L for CMC and MMC respectively.

This extended study clearly demonstrates the Cu(II) scavenging efficiency of MMC and CMC. The high uptakes attained combined with the alkaline buffering properties of MMC and CMC confirms the considerable potential for the neutralisation and detoxification of highly concentrated acidic effluents (e.g. copper etching fluids or acidic mining effluents). This merits further kinetic and adsorption equilibrium studies to establish if MMC and CMC are as effective for the removal of other metals e.g. the highly toxic Hg(II) and Pb(II) from concentrated solutions. Furthermore, it may be possible to recover Cu(II) in a concentrated form or immobilise and retain other toxic metal metals using MMC and CMC.
5.3.3.1 Evolution of pH

The evolution of pH was monitored for MMC, CMC, chitin and chitosan as the initial Cu(II) concentration was increased from 100 to 1000 mg/L. The results are shown in Figure 5.12.

A sudden increase in pH was observed on contact with MMC, CMC, chitin and chitosan from 4.5 to 8.6, 9.8, 5.8 and 9.7 respectively at 100 mg/L (Figure 5.12). This was attributed to the dissolution of CaCO₃ from the carapace and residual NaOH on the chitosan after deactylation. At this pH, the combined processes of sorption and precipitation will be contributing to the overall Cu(II) removal. Thereafter, as concentration increases, there was a corresponding decrease in pH to 6.2, 7.5, 4.9 and 7.7 at 1000 mg/L for MMC, CMC, chitin and chitosan respectively (Figure 5.12). This decrease in pH was attributed to ion exchanges between Cu(II) and protons from mildly acidic functional groups (e.g. amines and carboxyls) as Cu(II) out competes for metal binding sites. This trend was also observed for the extended concentration studies (results not shown).
5.3.4 Effects of concentration (pH controlled)

As for contact time, pH was controlled to restrict precipitation and assess the influence of pH on overall Cu(II) removal. Figure 5.13 shows (a) percentage removal and (b) specific uptake as the Cu(II) concentration was increased from 100-1000 mg/L.

Figure 5.13: Effects of initial concentration and pH on Cu(II) removal by MMC, CMC and Chitin, pH$_i$ = 4.5 and pH controlled between 4.3-4.7, V = 100 ml, T = 20 $^\circ$C ± 2 $^\circ$C, 5 grams, 250-800 $\mu$m particle size. All studies 60 minutes contact time. These studies were not conducted for chitosan.
With the pH controlled, the highest removal efficiencies were 86.3, 82.1 and 53.1% for MMC, CMC and chitin at 500, 1000 and 500 mg/L respectively (Figure 5.13a). While the Cu(II) uptakes were 11.7, 10.2 and 5.3 mg/g for MMC, CMC and chitin respectively. In effect, with pH controlled, the maximum removal efficiencies decreased by 9.7, 16.6 and 47.4% while the uptakes decreased by 5.2, 9.5 and 1.1 mg/g for MMC, CMC and chitin respectively. Again it is worth noting that the uptakes of Cu(II) by MMC and CMC appears to be directly proportional to initial concentration (Figure 5.13b).

In summary, the order of removal efficiencies and specific uptakes for MMC, CMC and chitin with pH controlled were MMC>CMC>chitin

This decrease in removal efficiencies and Cu(II) uptake by MMC, CMC and chitin was attributed to the lack of precipitation. Moreover, these studies also demonstrate the large variability in the Cu(II) sequestering potential of MMC, CMC, chitin and chitosan. Therefore, the effective removal of Cu(II) is highly dependant on the initial concentration and solution pH. This variability was attributed to differences in the physical and chemical characteristics of the materials (e.g. surface areas, porosity, structural stability and functionality) due to material preparation and conditioning processes.

The results concur with other studies with chitin and chitosan derivatives for Cu(II) sorption of as a function of concentration (Muzzarelli, 1973; 1989). Guibal et al., (1994) proposed that at low concentrations, metals are rapidly adsorbed to high energy binding sites on chitinous materials (e.g. amine and sulphur groups) as the concentration increases these rapidly become saturated and adsorption shifts to lower energy sites (e.g. hyroxides) resulting in less efficient removal. The results also concur with a later study by Guibal et al. (1995) evaluating the effects of pH on metal sorption by chitin and chitosan.
5.3.5 Dilute concentrations

Although commercial adsorbents e.g. activated carbons and ion-exchange resins can be effective for metal removal at low to medium concentrations (e.g. 20-100 mg/L), some of them can be ineffective at lower concentrations (e.g. 1-20 mg/L). Therefore, MMC and CMC were compared with chitin and chitosan for the removal of Cu(II) from the 1-50 mg/L range. The results are shown in Figure 5.14.

Figure 5.14: Removal of Cu(II) by MMC, CMC, chitin and chitosan (a) pH \(I = 4.5\) and no pH control and (b) MMC, CMC and chitin pH controlled between 4.3-4.7, \(V = 100\) ml, \(T = 20^\circ\)C ± 2 \(^\circ\)C, 5 grams, 250-800 \(\mu\)m particle size. Data for MMC and CMC (no pH control) was presented in Chapter 4 and are used here for comparison.
Without pH control, the removal of Cu(II) was highly efficient, particularly for chitosan (Figure 5.14a) and the final concentrations were maintained well below the current legislation requirement for Cu(II) in drinking water (Table 5.2).

### Table 5.2: Dilute Cu(II) concentrations studies (pH = 4.5 and no pH control)

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>Final concentration (mg/L)</th>
<th>a EEC (mg/L)</th>
<th>b US EPA (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.47</td>
<td>0.34</td>
<td>0.58</td>
</tr>
<tr>
<td>5</td>
<td>0.16</td>
<td>0.22</td>
<td>0.49</td>
</tr>
<tr>
<td>10</td>
<td>0.11</td>
<td>0.69</td>
<td>0.28</td>
</tr>
<tr>
<td>20</td>
<td>0.56</td>
<td>0.72</td>
<td>0.45</td>
</tr>
<tr>
<td>50</td>
<td>0.29</td>
<td>0.12</td>
<td>0.47</td>
</tr>
</tbody>
</table>

**Notes:** a EEC and b US EPA maximum contaminant limits in drinking water

When the pH was controlled to restrict precipitation, the final concentrations were still maintained below the legislation limits for MMC, CMC and chitin (Figure 5.14b and Table 5.3) suggesting the removal was solely by sorption processes.

### Table 5.3: Dilute Cu(II) concentration studies (pH = 4.5 and controlled to 4.3-4.7)

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>Final concentration (mg/L)</th>
<th>a EEC (mg/L)</th>
<th>b US EPA (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.39</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>5</td>
<td>0.53</td>
<td>0.39</td>
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<tr>
<td>10</td>
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<td>20</td>
<td>0.19</td>
<td>0.31</td>
<td>0.15</td>
</tr>
<tr>
<td>50</td>
<td>0.38</td>
<td>1.04</td>
<td>0.47</td>
</tr>
</tbody>
</table>

**Notes:** a EEC and b USEPA maximum contaminant limits in drinking water
These results compare favourably with those reported by Muzzarelli *et al.* (1989, 1999) using cross-linked chitins and chitosan and (Mcafee *et al.*, 2001) using chitin and chitosan for the removal of Cu(II) and other metals at trace concentrations.

Although the removal of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC at concentrations ranging from 1-50 mg/L was already established in Chapter 4 (see Figure 4.7). In these studies, both MMC and CMC were shown to compare favourably with the more expensive commercial adsorbents chitin and chitosan. In addition to this, the removal of Cu(II) from acidic solutions was confirmed (Table 5.3). These results clearly demonstrate the effectiveness of MMC and CMC for the removal of Cu(II) at dilute concentrations. Again this demonstrates the potential of MMC and CMC for applications as a polishing stage or a complimentary process with existing more expensive water treatments.
5.3.6 Effects of particle size

The choice of particle size is an important consideration when using biosorbent materials for the sorption of metals (Vijayaraghavan et al., 2004; 2005a). For example, it is preferable to use large particles for column operations, as small particles cause hydrodynamic flow restrictions and back pressures (Volesky, 2004). Also, smaller particles may not endure the acid and alkaline solutions used for metal recovery and regeneration of materials (Guibal et al., 1995). Figure 5.15 shows the Cu(II) removal by MMC, CMC, chitin and chitosan as particle size decreases from >2000µm to <250 µm.

![Figure 5.15: Effect of particle size on Cu(II) removal. Contact time 60 minutes, C<sub>i</sub> = 500 mg/L, pH<sub>i</sub> = 4.5 and controlled to 4.3-4.7, V = 100 ml, T = 20 °C ± 2 °C, 5 grams. Data for MMC was presented in Chapter 4 and used here for comparison. Studies with chitosan were conducted before establishing the effects of pH on structural stability.](image)

In general, as the particle size decreases there was a corresponding increase in Cu(II) removal (Figure 5.15). MMC removed 89.4% Cu(II) with <250µm, steadily decreasing to 11.5% at the >2000µm size fraction. CMC was only available at the 250–800µm particle size and removed 84.0%. This increase in uptake with decreasing particle size was also observed by Evans et al. (2002) and Vijayaraghavan et al. (2006) using crab shell for the removal of Cd(II) and Cu(II).
This trend was also observed for chitin, with 67.8% Cu(II) removal decreasing to 16.0% for <250µm and >2000µm respectively. However, a rather different trend was observed for chitosan with removal efficiencies of 31.5, 67.7, 72.1 and 69.1% observed for <250, 250–800, 800–2000 and >2000µm respectively (Figure 5.15). Findon et al., (1993) and Guibal et al., (1999) reported similar results for chitosan flakes with small variations in Cu(II) removal as particle size decreased from 1000µm to 210µm. These authors proposed that the number, distribution and accessibility of Cu(II) to amine groups were more important than the surface area.

Accessibility of metals to amine groups on chitosan is largely dependant on the degree of deacetylation and residual crystallinity (Guibal, 2004). As the chitosan used for these studies is ~87% deacetylated, has a higher N content and more open porous structure (depending on the pH) than MMC, CMC and chitin (Table 5.1 and Figure 5.5b) this could account for the Cu(II) removal observed for chitosan regardless of particle size (Figure 5.15). However, as the pH was controlled in these studies, the structure may be degraded and uptake to amine groups is not the predominant removal mechanism.

According to McKay, (1984) the uptake of metals from solution by porous materials generally involves four consecutive steps: (1) Mass transfer to the boundary film layer surrounding particles, (2) Metal transfer over the boundary film layer and adsorption to metal binding sites or precipitation at external surfaces, (3) Intra-particle diffusion of metals and (4) adsorption or micro-precipitation on interior surfaces.

In general, steps (1) and (2) are relatively fast compared to steps (3) and (4) if sufficient agitation is provided to overcome external mass transfer resistance at the boundary film layer.
The increase in uptake with decreasing particle size suggests that Cu(II) is preferentially adsorbed onto external surfaces. This hypothesis was assessed using qualitative SEM-EDAX micro-analysis (Figure 5.16).

**Figure 5.16:** SEM-EDAX micro analysis of Cu(II) distribution in MMC, CMC, chitin and chitosan particles (250-800µm). Treated particles contacted with 500 mg/L Cu(II) solutions for 60 minutes, pH\textsubscript{i} = 4.5 and controlled to 4.3-4.7, V = 100 ml, T = 20 °C ± 2 °C.

These images clearly show the formation of adsorbed Cu(II) clusters at the external surfaces of MMC and CMC confirming Steps (1) and (2) had occurred. This accumulation of Cu(II) at particle surfaces suggests intra-particle diffusion is a rate limiting step. The compact structure and high crystalline content (CaCO\textsubscript{3}) of MMC and CMC could be restricting the diffusion of Cu(II) into internal pores spaces (see Figures 5.2 and 5.3). This hypothesis was evaluated more rigorously using an intra-particle diffusion kinetic model and the results are presented and discussed in Chapter 7.
The chitin flakes appear to have Cu(II) distributed homogenously through the entire particle, indicating that all the steps of the sorption process had taken place (Figure 5.16). This means that all the Cu(II) binding sites could be occupied and would account for the abrupt decrease in uptake observed for chitin at concentrations >500 mg/L (Figures 5.10a and b). This further supports the hypothesis that intra-particle diffusion is rate limiting for MMC and CMC as most of the CaCO₃ would be removed from chitin by HCl during extraction from the Cancer pagurus (see Figure 5.1).

While the chitosan particles show a clear Cu(II) concentration gradient extending from the outer edges towards the centre (Figure 5.16). This accumulation and distribution of Cu(II) was also observed by Eiden et al. (1980) and Dzul-Erosa et al. (2001) using chitosan powder and Suder and Wightman (1983) using crab chitin and chitosan for the removal of Cr(III), Cd(II) and Zn(II) from aqueous solutions. These authors concluded that a combination of nodular formation, adsorption and absorption accounts for the total metal uptake. However, this distribution of metal was not observed by Benguella and Benaissa (2002) using chitosan flakes of similar size for the sorption of Cd(II).

As these studies were conducted using a contact time of 60 minutes and Cu(II) concentration of 500 mg/L, the equilibrium uptakes may not have been achieved for MMC, CMC and chitosan. Therefore this merits further investigations using higher Cu(II) concentrations (e.g. 3000-4000 mg/L) and longer contact times (4 to 24 hours), particularly for MMC and CMC. These extended studies combined with further SEM-EDAX micro-analysis would confirm or eliminate intra-particle diffusion as a rate limiting step. It would also be interesting to clarify if similar sorption processes are responsible for the uptake of Hg(II), Pb(II) and Zn(II) by MMC.
5.3.7 Effects of mass loading

The final parameter evaluated was the effects of mass loading. These types of studies provide useful information for optimisation of biosorbents at the industrial scale (Volesky, 2004). Figure 5.17 shows percentage removal and specific Cu(II) uptake by MMC, CMC and chitin as the mass was increased from 1 to 20 grams. Initial concentration was 1000 mg/L to identify the saturation of materials.

![Figure 5.17: Effects of mass loading on Cu(II) removal (a) percentage removal and (b) specific uptake, contact time 60 minutes, C_i = 1000 mg/L, pH_i = 4.5 and no pH control, V = 100 ml, T = 20 °C ± 2 °C, particle size 250-800 µm. These studies were not conducted for chitosan.](image-url)
In general, as MMC and CMC mass were increased there was a corresponding increase in percentage removal (Figure 5.17a). This was expected due to the increase in surface area and metal binding sites. The highest removal efficiencies obtained by MMC and CMC were 98.3 and 99.0 % for 20 and 10 grams respectively. Similar removals were obtained by Evans et al. (2002) and Vijayaraghavan et al. (2005) using crab particles of the same size range and similar experimental conditions. However, this trend was not observed for chitin and the best removal efficiency obtained was 44.0 % with 2 grams and thereafter removal efficiency decreased abruptly.

The highest uptakes were 18.1, 23.6 and 37.8 mg/g for MMC, CMC and chitin with 5.0, 2.0 and 1.0 grams respectively (Figure 5.17b). Thereafter, uptake decreased steadily with increases in mass. The rapid uptake obtained for 1 g of chitin was attributed to the small surface area and lower N content (see Chapter 5 Table 5.1). At the initial concentration used, uptake of Cu(II) by chitin would occur rapidly until all binding sites are occupied and the particles become saturated. These results concur with Muzzarelli et al. (1989) and Sag and Aktay (2000; 2002), who found that one-gram of chitin provided the maximum uptakes of Cu(II) and Cr(VI) from aqueous solutions. This also supports the hypothesis that chitin was saturated with Cu$^{2+}$ in the previous section (Figure 5.16).

A contrary explanation can be offered for the uptakes observed for MMC and CMC because of the larger surface areas and mixed functionality (Table 5.1). As the mass is increased the number of metal binding sites increases, resulting in a decrease in Cu(II) uptake mg/g assuming saturation has not occurred. In summary, the optimum mass loadings to obtain the highest removal efficiencies were 20, 10 and 2.0 grams for MMC, CMC and chitin respectively while the highest uptakes were obtained with 5, 2 and 1 gram for MMC, CMC and chitin respectively.
5.4. CONCLUSIONS

Chitinous materials MMC, CMC, chitin and crab chitosan were compared for the removal of Cu(II). Batch adsorption studies were used to evaluate the effects of contact time, initial concentration, pH, particle size and mass loading. A number of conclusions were made and these are summarised below.

1. The removal of Cu(II) by MMC, CMC, chitin and chitosan was rapid and highly dependant on initial concentration, pH and the physical and chemical characteristics of the materials.

2. With no pH control, chitosan was the most efficient material at low concentrations with >99.5 % removal up to 200 mg/L. MMC and CMC compared favourably with chitosan, 99.0 % removal over the 1-1000 mg Cu(II) /L range with or without pH control. Chitin was efficient 93.8 % over 1-100 mg Cu(II) /L range but less efficient (37.0%) over the 100-1000 mg Cu(II) /L range with or without pH control.

3. With no pH control, sorption and precipitation accounted for approximately 80.0 and 20.0 % respectively of the total Cu(II) removal by MMC and CMC. While the Cu(II) removal by chitin was hardly effected by pH (decrease of 5.0 %).

4. With pH controlled (4.3-4.7), Cu(II) uptake by chitosan decreased due to dissolution and protonation of functional groups causing electrostatic repulsion.

5. MMC, CMC, chitin and chitosan were all effective for the removal of Cu(II) at low concentrations (1–50 mg/L) and residual concentrations were maintained below the current legislation requirements for drinking water (2.0 mg/L).
6. In general, removal efficiency increased as mass loading increased, but increasing mass at a fixed Cu(II) concentration decreases uptake (mg/g) until saturation occurs. Chitin achieved the highest Cu(II) uptake with a mass loading of 1 gram.

7. SEM-EDAX micro-analysis revealed that Cu(II) uptake by MMC and CMC was predominantly via surface adsorption and precipitation and chitin and chitosan by adsorption, precipitation and intra-particle diffusion.

In conclusion, MMC and CMC were efficient for the removal of Cu(II) over the 1-4000 mg/L range and compared well with chitin and chitosan. The alkaline nature of MMC and CMC offers potential for the detoxification and neutralisation of acidic metal bearing effluents. The main Cu(II) removal mechanisms were sorption and precipitation depending on pH, initial concentration and material conditioning (Figure 5.18).

Figure 5.18: Proposed Cu(II) removal mechanisms by MMC, CMC, chitin and chitosan in these studies

To extend the assessment of MMC and CMC, Chapter 6 presents results from an inter-comparison with commercial metal adsorbents Darco® and Norit® activated carbons and Dowex® highly acidic ion-exchange resin beads for the removal of Cu(II).
CHAPTER 6 INTER-COMPARISON OF COMMERCIAL SORBENTS
In Chapter 5, MMC and CMC were compared with crab chitin and chitosan for the removal of Cu(II) from aqueous solutions. Chitin was the least efficient material, while MMC and CMC compared well with chitosan and were effective in acidic solutions over a larger concentration range 1-4000 mg/L. To extend the assessment of MMC and CMC, this Chapter presents results from an inter-comparison with commercial adsorbents, Darco® and Norit® activated carbons and Dowex® 50W ion-exchange resin beads. Each adsorbent was assessed by batch adsorption studies using the same experimental parameters applied for MMC, CMC, chitin and chitosan in Chapter 5.

6.1. INTRODUCTION

Throughout history, carbon rich materials e.g. wood and coal have been used as sorbents for the removal of colour, taste and odour from aqueous media (Toles et al., 1997). In modern water treatment systems, commercially produced carbons called “activated carbons” are used to remove dissolved metals. Precursor materials such as lignite and peat are heat treated (600-1000 °C) and chemically activated (e.g. nitric or phosphoric acids) resulting in highly porous products with large reactive surface areas (Blazewicz et al., 1999; Johns et al., 1999; Takashi, 2000). The effective uptake of metals is related to the number and distribution of oxygen containing functional groups (e.g. carbonyls) on carbon surfaces (Streat et al., 2001; Saha et al., 2001; Strelko et al., 2002).

Recently, activated carbons produced from industrial (Ramirez et al., 2000; Curkovic et al., 2001) and agricultural wastes (Toles and Marshall 2002; Wilson et al., 2005) have been shown to be effective for the removal Cd(II),Cu(II), Pb(II), Ni(II) and Zn(II) from aqueous solutions.
Ion-exchange resins can be highly efficient and selective for the removal of dissolved metals even at sub mg/L concentrations (Saha et al., 2000; Kiefer and Holl 2001; Pehlivan and Altun, 2005). However, their applications are often limited due to organic fouling, degradation, oxidation and high costs of regeneration and eluting chemicals (Tels, 1996, Rorrer, 1998). A concise review covering the history and development of commercial ion exchange resins was given by Abrams and Millar (1997).

The aim of this Chapter is to extend the assessment of MMC and CMC. The Cu(II) removals achieved by MMC and CMC in Chapters 4 and 5 were compared with those obtained by, Darco® and Norit® activated carbons and Dowex® 50W highly acidic ion-exchange resin beads. Each commercial sorbent was evaluated for removal of Cu(II) using the same experimental conditions and parameters used for MMC and CMC in Chapter 5.

6.2. MATERIALS AND METHODS

- MMC and CMC

MMC and CMC were used at the 250-800μm particle size.

- Activated carbons

Darco® acid-washed and steam-activated carbon (granular form, 20-40 mesh size, 420-800μm) was obtained from Aldrich, UK. This carbon is derived from lignite coal and designed for general purpose water purification processes e.g. removal of tastes, odours and colours (Darco® Technical Data Sheets). Norit® needle pellets Aldrich, UK (2-2.8 mm length, 0.8 mm diameter) derived from peat, chemically activated with phosphoric acid and designed specifically for the purification of potable water (Norit® Technical Data Sheets). Both carbons were used as supplied with no additional treatment.
• **Ion-exchange resin**

Dowex® 50W strongly acidic ion-exchange resin (spherical bead form, 20-50 mesh size; 0.30-0.85 mm; 4% cross-linked with divinylbenzene; with a cation exchange capacity of 1.8 meq / L (Dowex® Technical Data Sheets). The resin was obtained from (Aldrich, U.K) and used as supplied with no additional treatment.

• **Material characterisation**

Methods used to physio-chemically characterize MMC, CMC, Darco®, Norit® and Dowex® ion-exchange beads were described in Chapter 3 (see section 3.2 and Table 3.1).

• **SEM-EDAX**

SEM-EDAX micro-analysis was used to determine Cu(II) distributions in raw materials, and those contacted with Cu(II) solutions.

• **Batch adsorption studies**

Batch studies with the commercial sorbents were performed using the same experimental conditions applied for MMC and CMC in Chapter 5. All studies were done in triplicate and the means presented.

• **Metal solutions and chemical analysis**

Cu(II) solutions were prepared with analytical grade CuSO₄ (Aldrich, U.K). The residual Cu(II) concentrations were determined by AAS using the same methods described in Chapter 5 (see Metal solutions and chemical analysis page 106).
• Control of solution pH

Solution pH was controlled (when required) using the same procedure described previously (see Chapter 5 section 5.3.4).

• Effects of pH with Dowex® 50W resin

Due to the highly acidic nature of the Dowex® 50W ion-exchange resin beads and the rapid release of H⁺ ions during Cu(II) uptake, it was extremely difficult to control the solution pH between 4.3-4.7. Therefore, in these studies no pH controlled experiments were conducted with the Dowex® 50W ion-exchange resin beads.
6.3. RESULTS AND DISCUSSION

6.3.1 Material characterisation

The physical and chemical characteristics of MMC, CMC, Darco®, Norit® activated-carbons and the Dowex® ion-exchange resin beads were presented and discussed in Chapter 3 (see sections 3.3 and 3.4, Figures 3.1, 3.6, 3.7, 3.8 and Tables 3.2, 3.3). A selection of key physical characteristics and the cost of materials are presented in Table 6.1 for reference during the discussion of results.

The main points to note are that the Darco® and Norit® activated carbons have larger surface areas and extensive macro and micro porosity compared to MMC, CMC and Dowex® resin beads. Also, the commercial sorbents are considerably more expensive than MMC and CMC. The average pore diameter of MMC (200-800 µm particle size) is approximately the same size as that of activated carbons used to remove dyes (Ward et al., 2004).

Table 6.1: Selected characteristics of MMC, CMC, Darco®, Norit® activated carbons and Dowex® 50W Ion-exchange resin beads

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET surface area (m²/g)</th>
<th>Particle size (µm)</th>
<th>Pore diameter (volume)</th>
<th>Pore diameter (area)</th>
<th>Cost (£ / Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMC</td>
<td>22.50</td>
<td>250-800</td>
<td>0.34c (µm)</td>
<td>0.21c (µm)</td>
<td>1.20a</td>
</tr>
<tr>
<td>CMC</td>
<td>33.40</td>
<td>250-800</td>
<td>ND</td>
<td>ND</td>
<td>8.00a</td>
</tr>
<tr>
<td>Darco®</td>
<td>455.00</td>
<td>420-840</td>
<td>0.33d (cm³g)</td>
<td>0.25d (cm³g)</td>
<td>30.30b</td>
</tr>
<tr>
<td>Norit®</td>
<td>780.00</td>
<td>2.80 L 0.80 D</td>
<td>0.34d (cm³g)</td>
<td>0.40d (cm³g)</td>
<td>28.60b</td>
</tr>
<tr>
<td>Dowex® 50</td>
<td>&lt; 0.02</td>
<td>300-850</td>
<td>ND</td>
<td>ND</td>
<td>61.60b</td>
</tr>
</tbody>
</table>

Notes: *Estimated values; *Aldrich U.K catalogue price 2003, L = length (mm), D = diameter (mm); ND = not determined *Ward et al., 2004, *Norit Americas technical data services.
6.3.2 Effects of contact time and pH

Commercial sorbents, Darco® and Norit® activated carbons and Dowex® 50W strongly acidic ion-exchange resin beads were compared with MMC and CMC for the removal of Cu(II) from aqueous solutions. Figure 6.1 shows the percentage removals as a function of contact time and pH.

![Graph showing effects of contact time and pH](image)

**Figure 6.1:** Effects of contact time and pH. (a) pH₁ = 4.5 and no control and (b) C₁ = 500 mg/L, pH₁ = 4.5 and controlled between 4.3-4.7, V = 100 ml, T = 20 °C ± 2 °C, 5 grams of sorbents. Values in legends are (pH₂) at 60 minutes. Data for MMC and CMC were presented in Chapter 5 and used here for comparison.
Without pH control, the removal of Cu(II) by CMC and Dowex® was fast and highly efficient; 98.8 and 95.7% respectively at 5 minutes (Figure 6.1 a). While the removal by Norit® and MMC was less rapid, the efficiency increased with contact time to >99.0 % by 20 minutes. Darco® was the least efficient commercial sorbent. The highest removal efficiencies achieved were 99.9, 99.5, 99.3, 98.6 and 27.2 % for Norit®, Dowex®, MMC, CMC and Darco® at contact times of 60, 60, 40, 40 and 40 minutes respectively (Figure 6.2a). This corresponds to Cu(II) uptakes of 9.9, 9.9, 9.9, 9.8 and 2.7 mg/g respectively.

With pH controlled, the removal of Cu(II) by Darco® and Norit® decreased to 17.9 % and 82.3 % at 5 and 40 minutes respectively (Figure 6.1 b). This corresponds to Cu(II) uptakes of 1.8 and 8.2 mg/g respectively. It is worth noting that after 40 minutes there was an abrupt decrease in removal efficiency by Norit® from 82.3 % to 24.0 %. This may be due to the occupation of all available metal binding sites at this concentration or electrostatic repulsion of Cu(II) at this pH range.

In summary, when compared with MMC and CMC from Chapter 5, the order of efficiencies with no pH control were Norit®>Dowex®>MMC>CMC> Darco®, and with pH controlled CMC>MMC>Norit® >Darco®.

Comparing removal efficiencies with and without pH control (Figure. 6.1) it can be concluded that sorption and precipitation processes account for approximately 70.0% and 30.0% and 83.0% and 17.0% of the total Cu(II) removal for Darco® and Norit® carbons respectively. While ion exchange accounts for the total Cu(II) removal by Dowex® 50 W resin beads. The higher removal efficiency of Norit® with respect to Darco® was attributed to the larger surface area and activation with phosphoric acid (Table 6.1).
These results are consistent with studies by Toles et al., (1999) and Wilson et al., (2005) comparing Darco®, Norit® and a carbon derived from peanut shell for Cu(II) removal. They concluded that Darco® was the least efficient carbon and attributed this to the smaller number of metal binding functional groups due to the steam activation process. While the phosphoric acid activated Norit® performed better due to the larger number of metal binding functional groups (e.g. oxygens) and higher negative surface charge density. The activation process, smaller surface area of Darco® (Table 6.1) and solution pH may explain the lower Cu(II) removals observed in these studies.

A similar comparative study by An et al. (2001) showed that carapace from Chinonecetes opilio exceeded the Cu(II) removal obtained by Dowex® 50W ion-exchange resin, powdered and granular activated carbons. Many other studies in the literature report similar uptakes of Cu(II) with low-cost biomass compared to that of commercial adsorbents (Bailey et al. 1999; Babel and Kurniawin 2003; Lloyd-Jones et al. 2004). It was concluded from this study, that Darco® was the least efficient commercial adsorbent (with or without pH control). While Norit® and Dowex® were marginally more efficient than MMC and CMC (with no pH control), MMC and CMC compare favourably and were more efficient in acidic solutions.

Alkaline deacetylation of crab-chitin produces chitosan and exposes more metal binding amino groups (Figure 5.5 and Table 5.1). The solution pH rapidly becomes alkaline during agitation with MMC and CMC particles (Figures 6.2a and b and Figure 6.3a). As carapace from the Cancer pagurus contains ~50% chitin, partial deacetylation of chitin and formation of chitosan at the outer surfaces of MMC and CMC particles may be taking place. This combined with micro precipitation on external surfaces may be contributing towards the effective removal of Cu(II) by MMC and CMC.
6.3.2.1 Evolution of pH

Figure 6.2 shows the evolution of pH during contact time with a Cu(II) concentration of 500 mg/L (a) and (b) when 5 grams of each sorbent were contacted with ultra-pure water with no Cu(II) present e.g. (controls).

![Figure 6.2](image)

**Figure 6.2:** Evolution of pH over time (a) 500 mg/L Cu(II), pH$_i$ = 4.5, V = 100 ml, T = 20 °C ± 2 °C, 5 grams and (b) 0 mg/L Cu(II) e.g. ultra-pure water, pH$_i$ = 7.4, V = 100 ml, T = 20 °C ± 2 °C, 5 grams of sorbents. Contact times 0-60 minutes for all studies. Data for MMC and CMC in (a) were shown in Chapter 5 and used here for comparison.
A steady increase in pH was observed for Norit® (Figure. 6.2a). This was attributed to leaching of organics and would result in the precipitation of Cu(II). While for Darco® there was a slight decrease in pH and attributed to acid washing (see section 6.2). This is also consistent with values given in technical data sheets. However, for Dowex® 50W resin, pH decreased rapidly from 4.5 to 2.1 indicating exchanges of H⁺ during the uptake of Cu(II) (Figure 6.2a). With no Cu(II) present (controls), pH increased rapidly on contact with Darco® and Norit® (Figure. 6.2 b) due to leaching of organics. The pH in the Dowex® 50W system decreased rapidly due to exchange of H⁺ ions.

Figure 6.3 shows SEM-EDAX elemental analysis of CMC before and after contact with 500 mg/L Cu(II) solutions. After contact with Cu(II), the Ca(II) peak is significantly reduced and a clear Cu(II) peak is present indicating the precipitation of copper on CMC surfaces and that ion exchanges between Ca(II) and Cu(II) may be occurring. SEM-EDAX elemental spectra for MMC, Darco®, Norit® and Dowex® all exhibit the same Cu(II) peaks with respect to raw materials (see Figures 1.1a -1.5a Appendix C).

![Figure 6.3: SEM-EDAX elemental spectra of CMC before (black line) and after (red line) 60 minutes agitation (350 rpm) with 500 mg/L Cu(II) solutions.](image)
6.3.3 Effects of concentration (no pH control)

Figure 6.4 shows the percentage Cu(II) removal and uptake by Darco® and Norit® activated carbons and Dowex® 50W ion-exchange resin beads as concentration was increased from 100-1000 mg/L.

Figure 6.4: Effects of initial Cu(II) concentration on (a) percentage removal and (b) specific uptake (mg/g). pH_i = 4.5 and no control, V = 100 ml, T = 20 °C ± 2 °C, 5 grams, 60 minutes contact time, (Values in legends are the pH at 1000 mg/L). Data for MMC and CMC were presented in Chapter 5 and are used here for comparison.
The Dowex® 50W ion-exchange resin was highly efficient removing >99.0 % of Cu(II) over the whole concentration range (Figure 6.4 a). While Norit® activated carbon was effective at lower concentrations, 99.9 % up to 200 mg/L, the efficiency decreased slightly to 92.0 % at 1000 mg/L (Figure 6.4 a). Darco® activated-carbon was efficient at 100 mg/L, removing 81.2 % Cu(II), then the efficiency decreased steadily with increasing concentration to 15.1% at 1000 mg/L. The highest removal efficiencies were 99.8, 99.8, and 81.2 % for Dowex®, Norit® and Darco® at 200, 500 and 100 mg/L respectively.

The specific uptake of Cu(II) by Norit® and Dowex® increased steadily as the initial concentration increased from 1.9 and 1.9 mg/g at 100 mg/L to 18.4 and 19.6 mg/g respectively at 1000 mg/L (Figure 6.4 b). While the uptake of Cu(II) by Darco® increased steadily between 100 and 200 mg/L and reached a maximum of 4.3 mg/g at 500 mg/L. It is also interesting to note that as observed for MMC, CMC and chitosan in Chapter 5, the Cu(II) uptakes by Norit® and Dowex® appear to be directly proportional to the initial concentration. Also the equilibrium uptakes were not reached at 1000 mg/L (Figure 6.4 b and Figure 5.10 b in Chapter 5).

In summary, when compared with the Cu(II) removal by MMC and CMC in Chapter 5, the order of removal efficiencies were Norit≥Dowex>CMC>MCC >Darco while the largest uptakes obtained were CMC>Dowex>Norit>MCC >Darco
6.3.4 Effects of concentration (pH controlled)

Figure 6.5 shows the percentage removal and specific uptake of Cu(II) by Darco® and Norit® activated carbons as the initial concentration was increased from 100-1000 mg/L with the pH controlled to 4.3-4.7.

Figure 6.5: The effects of initial Cu(II) concentration and pH on (a) percentage removal and (b) specific uptake (mg/g). pH = 4.5 and controlled to 4.3-4.7, V = 100 ml, T = 20 °C ± 2 °C, 5 grams, 60 minutes contact time. (Values in legends are the pH at 1000 mg/L). Data for MMC and CMC were shown in Chapter 5 and used here for comparison.
With the pH controlled between 4.3-4.7 to establish the maximum sorption rather than precipitation of Cu$^{2+}$, the removal efficiencies of Darco® and Norit® decreased by approximately 20.0 and 60.0 % respectively (Figure 6.5 a). The highest removal of Cu(II) was achieved for both carbons at a concentration of 100 mg/L with 29.9 and 40.4 % respectively. Thereafter, as the initial concentration increased, the removal efficiency decreased steadily to 6.0 % and 23.7 % at 1000 mg/L for Darco® and Norit® respectively.

Cu(II) uptake by Darco® increased slightly as the concentration increased from 0.6 mg/g at 100 mg/L up to a maximum of 1.2 mg/g at 1000 mg/L (Figure 6.5 b). While the Cu(II) uptake by Norit® increased steadily as the initial concentration increased from 0.8 mg/g at 100 mg/L to 4.9 mg/g at 1000 mg/L.

In summary, when compared with the Cu(II) removals achieved by MMC and CMC in Chapter 5, the order of efficiencies were MMC>CMC>Norit®>Darco® and the largest uptakes was CMC>MMC>Norit®>Darco®

As observed for the contact time studies, reduced uptake of Cu(II) by Darco® and Norit® reflects the absence of precipitation in these conditions. Comparing results obtained with and without pH control, the activated carbons show the greatest sensitivity to concentration and solution pH (Figures. 6.1b and 6.5). The variability in metal uptake by the Darco® and Norit® activated carbons has been attributed to different surface areas, surface charges, precursor materials and activation methods used (Streat et al., 2001; Chu, 2002; Ahmenda et al., 2004). While Seco et al. (1999) and Chu and Hashmin, (2000; 2003) proposed that at low initial concentrations Cu(II) is rapidly adsorbed to high energy binding sites on Darco® (e.g. carboxyls and hydroxyls), as the sites become saturated, adsorption shifts to lower energy sites with a decrease in uptake.
6.3.4.1 Evolution of pH

Figure 6.6 shows the evolution of pH for Darco®, Norit® and Dowex® 50W resin beads as the initial Cu(II) concentration was increased from 100-1000 mg/L.

![Evolution of pH](image)

**Figure 6.6**: Evolution of pH with increasing Cu(II) concentration. pH$_i$ = 4.5 and no control, T = 20 °C ± 2 °C, V = 100 ml, 5 grams of sorbent, 60 minutes contact time. Data for MMC and CMC were shown in Chapter 5 and are used here for comparison.

With the exception of Dowex® 50W resin beads, all the sorption systems show an abrupt increase in solution pH at low concentrations then a gradual decrease as the Cu(II) concentration increases (Figure 6.6). As the concentration is increased, Cu(II) starts to compete with the hydrogen ions for sorption sites on mildly acidic functional groups. Consequently, H$^+$ ions are released into the solution resulting in a decrease in the solution pH. This suggests that depending on the initial solution pH and Cu(II) concentration, ion exchange processes are responsible for a proportion of the total Cu(II) removal.

An ion-exchange model was used to test this hypothesis and quantify the contribution of ion-exchange to the overall removal of Cu(II) and Hg(II), Pb(II) and Zn(II) by MMC. The results from this study are presented and discussed in Chapter 7.
6.3.5 Dilute Cu(II) concentrations

Darco® and Norit® activated carbons and Dowex® 50W ion-exchange resin beads were assessed for the removal of Cu(II) at low concentrations (1-50 mg/L) and compared with the removals obtained by MMC and CMC in Chapter 5. The results are presented in Figure 6.7 and Tables 6.2 and 6.3.

Figure 6.7: Cu(II) removal from dilute concentrations (a) pH$_I$ = 4.5 and no control and (b) MMC, CMC, Darco®, and Norit®, pH$_I$ = 4.5 and controlled to 4.3-4.7. Contact time 60 minutes, V = 100 ml, T = 20 °C ± 2 °C, 5 grams. Data for MMC and CMC were presented in Chapter 5 and used here for comparison.
Without pH control, removal of Cu(II) was highly efficient, particularly for the Norit® activated carbon and Dowex® resin beads (Figure 6.7 a). The final concentrations were maintained below the legislation requirement for Cu(II) in drinking water (Table 6.2). However, efficiency of Darco® decreased rapidly as concentration increased >5.0 mg/L.

### Table 6.2: Dilute Cu(II) concentrations (pH<sub>i</sub> = 4.5 and no pH control)

<table>
<thead>
<tr>
<th>C&lt;sub&gt;i&lt;/sub&gt;(mg/L)</th>
<th>MMC</th>
<th>CMC</th>
<th>Darco®</th>
<th>Norit®</th>
<th>Dowex®</th>
<th>EEC (mg/L)</th>
<th>US EPA (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.47</td>
<td>0.34</td>
<td>0.46</td>
<td>0.02</td>
<td>0.08</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>5</td>
<td>0.16</td>
<td>0.22</td>
<td>1.85</td>
<td>&lt; 0.01</td>
<td>0.03</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>10</td>
<td>0.11</td>
<td>0.69</td>
<td>3.53</td>
<td>0.01</td>
<td>0.03</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>20</td>
<td>0.56</td>
<td>0.72</td>
<td>16.05</td>
<td>&lt; 0.01</td>
<td>0.02</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>50</td>
<td>0.29</td>
<td>0.12</td>
<td>38.85</td>
<td>0.10</td>
<td>0.02</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**Notes:** Entries in bold italics indicate where discharge limits have not been met.

With pH controlled, final concentrations were still below the limits for MMC, CMC and Norit® (Figure 6.7b and Table 6.3). While Darco® was only effective up to a concentration of 5 mg/L.

### Table 6.3: Dilute Cu(II) concentrations (pH<sub>i</sub> = 4.5 and controlled to 4.4-4.7)

<table>
<thead>
<tr>
<th>C&lt;sub&gt;i&lt;/sub&gt;(mg/L)</th>
<th>MMC</th>
<th>CMC</th>
<th>Darco®</th>
<th>Norit®</th>
<th>Dowex®</th>
<th>EEC (mg/L)</th>
<th>US EPA (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.39</td>
<td>0.22</td>
<td>0.97</td>
<td>0.81</td>
<td>ND</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>5</td>
<td>0.53</td>
<td>0.39</td>
<td>1.64</td>
<td>0.99</td>
<td>ND</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>10</td>
<td>0.54</td>
<td>0.32</td>
<td>2.63</td>
<td>0.55</td>
<td>ND</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>20</td>
<td>0.19</td>
<td>0.31</td>
<td>6.53</td>
<td>0.13</td>
<td>ND</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>50</td>
<td>0.38</td>
<td>1.04</td>
<td>28.62</td>
<td>0.93</td>
<td>ND</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**Notes:** Entries in bold italics indicate where discharge limits have not been met.
Comparing results obtained with and without pH control, it is clear that the combined processes of sorption and precipitation contributes towards the total Cu(II) removal with Darco® and Norit®. Therefore, when the pH is controlled between 4.3-4.7 there will be positively charged functional groups on the carbon surfaces causing electrostatic repulsion of Cu(II). Although Norit® carbon and Dowex® resin beads were the most efficient commercial sorbents at low Cu(II) concentrations, MMC and CMC compared well and were more effective for the removal of Cu(II) from acidic solutions.

6.3.6 Effects of pH

From the data presented in Figures 6.1 and 6.4 it is clear that the efficient removal of Cu(II) by MMC, CMC, Darco® and Norit® is highly dependant on the initial solution pH. This dependency is illustrated further in Figure 6.8 as pHI was increased from 1 to 5.

![Figure 6.8: Effects of the initial pH on the percent Cu(II) removal. C_i = 500 mg/L, V = 100 ml, T = 20 °C ± 2 °C, 5 grams of sorbents, contact time = 60 minutes. Values in the legend = pH_f at 60 minutes](image-url)
For all materials, the sorption edge lies in a narrow pH region (1-3 pH units) with the greatest Cu(II) removals observed between pH 2 and 5 (Figure 6.8). A number of suggestions have been proposed to explain this phenomenon for activated carbons. For example, Seco et al. (1999) reported that increasing pH reduces competition between H⁺ and Cu(II) ions for binding sites on Darco® activated carbons. While, Chu and Hashmin (2000) proposed that increasing the pH reduces the positive surface charge density of activated carbons by de-protonation of mildly acidic surface functional groups.

Similarly, Chen et al., (1996) and Chen and Lin (2001) reported that increasing solution pH significantly enhanced the removal of Cu(II) by Filtrasorb® 200 and 400 activated carbons. They attributed this to a reduction in the positive surface charge density (zeta potential) of the carbons and a decrease in the electrostatic repulsion of metal cations.

Furthermore, the precipitation of Cu(II) to the insoluble Cu(OH)₂ or CuCO₃ species occurs with MMC and CMC when solution pH >5 (see Figure 5.6a Chapter 5). Consequently, as the initial pH is increased, Cu(II) removal is increased by the combined mechanisms of adsorption, complexation and precipitation.

These removal trends are consistent with other studies using crab shells and activated carbons for the removal of Cu(II) and other heavy metals from aqueous solutions (Lee et al., 1997; Lee et al., 1998; An et al., 2001). These authors observed a significant increase in Cu(II) removal from 2.0 to 99.0 % as the solution pH was increased from 1.7 to 7. A proportion of this removal was attributed to the dissolution of CaCO₃ from the crab carapace followed by the formation of metal-carbonate complexes and adsorption to chitin fibres exposed at the outer surfaces of the particles.
To determine if these mechanisms were responsible for the uptake of Cu(II) by MMC in these studies, SEM-EDAX micro analyses were conducted to view the surfaces of MMC particles before and after exposure to 500 mg/L Cu(II) solutions (Figure 6.9).

Figure 6.9: SEM-EDAX micro analysis of MMC, 250-800 µm size (a) raw MMC, (b) contacted with 500 mg/L of Cu(II) for 60 minutes, pH₁ = 4.5 and no control, (c) Cu(II) micro-precipitates (d) EDAX elemental dot-map of particle shown in image (c).

Figure 6.9a shows chitin fibres exposed at the outer surfaces of raw MMC particles. Figures 6.9b and c show the formation of Cu(II) micro precipitates in discreet patches on the outer surfaces of the particles after contact with 500 mg/L Cu(II) solutions. While SEM-EDAX elemental analysis of the particle shown in Figure 6.9c clearly shows that Cu(II) is distributed evenly over the surfaces Figure 6.9d. These SEM images confirm that adsorption and micro-precipitation on MMC surfaces are major Cu(II) removal mechanisms in these studies.
6.4. CONCLUSIONS

Commercial sorbents Darco® and Norit® activated carbons and Dowex® 50W ion-exchange resin beads were evaluated for Cu(II) removal from single metal solutions and compared with the removal obtained by MMC and CMC in Chapter 5. A number of conclusions were made and these are summarised below.

1. With no pH control, Cu(II) removal by Dowex® 50W resin beads and Norit® activated carbon was fast and efficient, 99.0 % by 20 minutes, over the 100-1000 mg/L range. Darco® was effective at lower concentrations, 82.0 % at 100 mg/L, but removal decreased with increasing concentration with or without pH control.

2. With pH controlled the efficiency of Darco® and Norit® decreased by approximately 20.0% and 60% respectively due to lack of precipitation and electrostatic repulsion. MMC and CMC compared favourably with the most efficient commercial sorbents Dowex® 50W and Norit® and were more efficient in acidic solutions.

3. MMC, CMC, Norit® and Dowex® 50W were all effective for the removal of Cu(II) from dilute concentrations and final concentrations were below the current legislation limits for potable water. Darco® was only effective at concentrations < 5 mg/L.

4. The removal of Cu(II) by Darco® and Norit® was highly dependant on the initial pH, with the best removals obtained as pH increased from 3 to 5.

5. Based on results from these studies, it was concluded that the main Cu(II) removal mechanisms were sorption, precipitation, complexation and ion-exchange depending on the initial concentration and solution pH.
These inter-comparison studies showed that MMC and CMC were comparable to and could sometimes exceed the Cu(II) removals obtained with more expensive commercial sorbents. MMC and CMC were also particularly effective in acidic solutions due to the buffering capacity obtained by the dissolution of CaCO₃. Although MMC was marginally less efficient than CMC in some cases, the production of MMC is more cost effective and less labour intensive to prepare from the raw carapace (Table 6.1).

Therefore, given the metal removals obtained by MMC in Chapters 4, 5 and 6, MMC was selected for kinetic and adsorption isotherm modelling studies to quantify sorption rates and the equilibrium uptake capacities of MMC for Cu(II), Hg(II), Pb(II) and Zn(II). In addition, an ion-exchange model was tested to determine the contribution of ion-exchange to the overall metal removal process. The results from these studies are presented and discussed in Chapter 7.
7. CHAPTER 7 SORPTION KINETICS AND EQUILIBRIUM
In Chapters 5 and 6, MMC and CMC were compared with chitin, chitosan, and commercial sorbents Darco® and Norit® activated-carbons and Dowex® 50W ion-exchange resin for the removal of Cu(II). MMC and CMC were shown to compare favourably and were superior in acidic solutions. This Chapter extends the assessment of MMC by establishing the sorption rates and equilibrium uptakes of Cu(II), Hg(II), Pb(II) and Zn(II) from single metal solutions. Sorption kinetics was evaluated using the pseudo-first order, pseudo-second order models and an intra-particle diffusion models. The metal uptakes at equilibrium were quantified using Langmuir, Freundlich and Redlich-Peterson adsorption isotherm models. The validity of these models was assessed with the Chi-square statistic test. Also, an ion-exchange model was tested to evaluate the contribution of ion-exchange to the overall metal removals.

7.1. INTRODUCTION

The sorption kinetics and equilibrium uptake are fundamental considerations when evaluating biosorbents for the removal of metals from aqueous solutions (Volesky, 1990, 2003; Wase and Forster, 1997). Experimental data from small-scale batch adsorption studies can be used to provide sorption rates (Benguella and Benaissa, 2002; Evans et al., 2002; Loderio et al., 2006), time to reach equilibrium, (Sag and Aktay, 2000; Chu and Hashmin, 2003) and produce predictive models for larger scale column studies (Kratochvil et al., 1997; Lee et al., 1998; Vijayaraghavan et al., 2004; Naja and Volesky, 2006).

A number of mathematical models have been developed to predict sorption kinetics and equilibrium uptake of metals, each with varying degrees of complexity (Ho and McKay, 1998; Volesky, 2003; Ho, 2006). Excellent reviews of some single and multi-component models were given by Yu and Neretnieks (1990) and Volesky (2003).
The two most commonly applied models are the adsorption isotherms developed by Freundlich (1907) and Langmuir (1918). Although these models are not capable of describing the sorption mechanisms, they can be easily applied to batch experimental data and only involve two isotherm parameters (Allen et al., 2004).

This Chapter presents results from a series of batch adsorption studies designed to establish the sorption rate kinetics and equilibrium uptake capacities of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC. Experimental data from single metal-MMC sorption systems were evaluated using the first order and pseudo-second order kinetic models of Lagergren (1898) and Ho and Mackay (1999) and the intra-particle diffusion model developed by Weber and Morris (1962). The equilibrium uptakes were determined using the Langmuir (1918), Freundlich (1907) and the Redlich-Peterson, (1959) adsorption isotherm models. In addition to these, the ion-exchange model proposed by Sciban and Klasnja (2004) was tested to evaluate the contribution of ion-exchange to overall metal removal.

7.2. MATERIALS AND METHODS

- MMC

Based on the lower cost and the effective removals of Cu(II), Hg(II), Pb(II) and Zn(II) obtained by MMC in Chapters 4 and 5. MMC was selected for these studies and used at the 250-800 µm particle size.
Batch studies

Sorption kinetics were determined by agitating 0.25 grams of MMC with 100 mg/L single metal solutions and varying contact times from 30 to 1440 minutes. Due to the increase in pH on contact with MMC, the pH was maintained at 4.3-4.7 for Cu(II) and between 5.0-6.0 for Hg(II), Pb(II) and Zn(II) to restrict precipitation (Figure 7.1).

![Graphs of Cu(II), Hg(II), Pb(II), Zn(II) removal as a function of initial pH](image)

**Figure 7.1:** Precipitation of Cu(II), Hg(II), Pb(II) and Zn(II) as a function (pH<sub>i</sub>) in Ultra-pure water with no MMC. C<sub>i</sub> = 100 mg/L, V = 100 mL, T = 21 °C ± 2 °C, agitation rate 350 rpm.

Sorption isotherms for each metal were obtained by agitating various masses of MMC (0.001-4 grams) with 100 mL of 100 mg/L metal solutions. The contact time was fixed at 1440 minutes to allow sufficient time to attain equilibrium. The pH was not adjusted and the initial solution pH<sub>i</sub> was 4.2, 4.4, 4.9 and 4.7 for Cu(II), Hg(II), Pb(II) and Zn(II) respectively.
The release of Na(I), K(I), Ca(II) and Mg(II) from MMC (e.g. major exchangeable cations) was determined by adding 0.4 grams to 100 mL Ultra pure water (controls), or 100 ml of single metal solutions 100 mg/L and agitating for 1440 minutes. The (pHf) of the controls and metal solutions were adjusted to 2.0, 3.3, 3.3 and 3.5 for Cu(II), Hg(II), Pb(II) and Zn(II) respectively to restrict the precipitation of metals. All batch experiments were conducted in triplicate at room temperature (20 °C ± 2 °C) using an agitation speed of 350 rpm.

- **Metal solutions and analysis**

  Stock K(I), Na(I), Ca(II), Cu(II), Hg(II), Mg(II), Pb(II) and Zn(II) solutions of 100 mg/L were prepared by dissolving analytical grade metal salts (Aldrich U.K) in ultra-pure water (Millipore Direct 3 System). The solution pH was adjusted (when required) by the drop-wise addition of 1.0 M HCl or 1.0 M NaOH.

  After the required period of contact between metal solutions and MMC, the final pH (pHf) was recorded. The solutions were then vacuum filtered (Whatman GF/A; pore size 1.6 µm), acidified (pH ~ 2) with 1.0 M HCl and stored at 2.0 °C until analysis. The metal concentrations in the filtrates were determined by FAAS or Flame Photometry as described in Chapter 2 (see section 2.4.9). The metal uptake q (mg/g, mmol / g / MMC) from each sorption system was determined using the mass balance equation given in Chapter 2 (Equation 2.4).
7.3. SORPTION KINETICS

The sorption rate kinetics was evaluated with adaptations from the first-order model of Lagergren (1898), pseudo-second-order model of Ho and McKay (1999) and the intra-particle diffusion model proposed by Weber and Morris (1962).

7.3.1 First-order model

The pseudo-first-order model of Lagergren (1898) can be used to describe the sorption of solid / liquid systems based on the solid capacity (Mckay et al., 1999)

\[
\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{7.1}
\]

\(q_e\) and \(q_t\) = metal uptake at equilibrium and time \(t\), respectively (mg/g or mmol/g)
\(k_1\) = rate constant of first-order sorption (1 / min).

Integrating equation 7.1 for the boundary conditions \(t = 0\) to \(t = t\) and \(q_t = 0\) and \(q_t = q_e\), the integrated form becomes:

\[
\log \left( \frac{q_t}{q_e - q_t} \right) = \frac{k_1 t}{2.303} \tag{7.2}
\]

Equation 7.2 can be rearranged to provide linear Equation 7.3 and plots of \(\log (q_e - q_t)\) versus \(t\) should produce a straight line and indicate the applicability of this model.

\[
\log (q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{7.3}
\]
7.3.2 Pseudo-second-order model

The pseudo-second-order model by Ho and McKay (1998) is based on the sorption capacity of the solid phase and is often applied if the pseudo-first-order equation fails.

\[ \frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \]  

(7.4)

Integrating equation 7.4 for the boundary conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = 0 \) provides Equation 7.5. This is the integrated rate law for a pseudo-second-order reaction.

\[ \frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \]  

(7.5)

Where \( q_e = \) metal uptake at equilibrium (mg/g or mmol/g) and \( k_2 = \) pseudo-second-order sorption rate constant (g/mg/min).

Equation 7.5 can be rearranged to obtain Equation 7.6 and the values of \( h \) and \( q_e \) can be determined from the slope and intercept of a linear plot of \( t/q_t \) versus \( t \)

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \]  

(7.6)

\[ h = k_2 q_e^2 \]

Where \( h = \) the initial sorption rate (mg/g/min).
7.3.3 **Intra-particle diffusion model**

Webber and Morris (1962) developed a model to evaluate rate-limiting diffusion processes for the sorption of pollutants from wastewater (Equation 7.7). They proposed that the rate of intra-particle diffusion can be calculated from a plot of $q_t$ versus $t^{1/2}$.

$$q_t = k_{id} \sqrt{t}$$  \hspace{1cm} (7.7)

Where:

$k_{id}$ = intra-particle diffusion rate constant (mg/g/min$^{1/2}$)

$q_t$ = metal uptake at any time (mg/g or mmol/g)

$\sqrt{t}$ = square root of time (min$^{1/2}$)

7.4. **SORPTION ISOTHERMS**

The most appropriate method to evaluate biosorbents for metal removal is by producing complete sorption isotherms (Volosky, 2003). Sorption isotherms provide equilibrium metal concentrations in the solution phase and solid phase. In addition to providing experimental and theoretical uptake ($q$), isotherms enable comparisons between biosorbents and provide useful information (e.g. biosorbent affinity and mass transfer characteristics) for optimising larger scale biosorption systems (Guibal, 2004).

Three frequently applied isotherm models were selected for these studies, the two-parameter Langmuir (1918), Freundlich (1907) and the three-parameter Redlich-Peterson (1959).
7.4.1 Langmuir adsorption isotherm

The Langmuir adsorption isotherm model (Langmuir, 1918) can be used to describe the sorption of solutes from solution (Ho and McKay, 1999) and is expressed as:

\[ q_e = \frac{q_{\text{max}} K_a C_e}{(1 + K_a C_e)} \quad (7.8) \]

\( q_e \) = metal uptake at equilibrium (mg/g or mmol/g /dry weight sorbent)

\( C_e \) = concentration of metal in solution at equilibrium (mg/L or mmol/L)

\( q_{\text{max}} \) = maximum uptake capacity for complete monolayer coverage (mg/g or mmol/g)

\( K_a \) = Langmuir constant related to energy of adsorption or affinity (L/g or L/mmol)

Equation 7.8 can be rearranged to provide the linear Equations 7.9 and 7.10 and the Langmuir constants (\( q_{\text{max}} \) and \( K_a \)) can be calculated from the slopes and intercepts.

\[ \frac{C_e}{q_e} = \frac{1}{q_{\text{max}} K_a} + \frac{C_e}{q_{\text{max}}} \quad (7.9) \]

\[ \frac{1}{q_e} = \frac{1}{(K_a q_{\text{max}})} \frac{1}{C_e} + \frac{1}{q_{\text{max}}} \quad (7.10) \]

A plot of \( \frac{C_e}{q_e} \) versus \( C_e \) from Equation 7.9 should provide a straight line with slope of \( \frac{1}{q_{\text{max}}} \) and an intercept of \( \frac{1}{(K_a q_{\text{max}})} \).
Alternatively, a plot of \( \frac{1}{q_e} \) versus \( \frac{1}{C_e} \) from Equation 7.10 should provide a straight line with slope of \( \frac{1}{(K_a q_{\text{max}})} \) and an intercept of \( \frac{1}{q_{\text{max}}} \).

According to Hall *et al.* (1966), the shape of the adsorption isotherm can be used to predict whether a sorption system is favorable or unfavorable in both batch adsorption and fixed bed systems. The features of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor \( (K_r) \) or equilibrium parameter using (Equation 7.11).

\[
K_r = \frac{1}{1 + K_a C_i}
\]

(7.11)

Where: \( K_r \) = dimensionless separation factor and \( C_i \) = initial concentration (mg/L or mmol/L)

The parameter \( K_r \) defines the shape of the isotherm in the following ways.

\( K_r > 1 \) Unfavourable sorption
\( K_r = 1 \) Linear
\( 0 < K_r < 1 \) Favourable sorption
\( K_r = 0 \) Irreversible sorption
7.4.2 Freundlich adsorption isotherm

The Freundlich isotherm model is the earliest known relationship describing the sorption system Freundlich (1907). This is a non-ideal empirical isotherm and unlike the Langmuir isotherm can be applied to describe sorption processes involving heterogeneous surfaces with different binding energies (Wang and Quin, 2005) and is expressed as:

$$q_e = k_f C_e^{1/n}$$  \hspace{1cm} (7.12)

Where $k_f$ and $1/n$ are the Freundlich isotherm constants, $k_f$ = the adsorbent capacity (mg/g or mmol/g) and $1/n$ = the adsorption intensity.

Equation 7.12 can be linearised by taking natural logs (ln) of both sides (e.g. Logs to the base e) and provides (Equation 7.13)

$$\ln(q_e) = \ln(k_f) + \frac{1}{n} \ln(C_e)$$  \hspace{1cm} (7.13)

The Freundlich isotherm constants ($k_f$ and $1/n$) can then be calculated from the slopes and intercepts of linear plots of $\ln(q_e)$ versus $\ln(C_e)$. 
### 7.4.3 Redlich-Peterson adsorption isotherm

The Redlich-Peterson isotherm contains three adjustable parameters and incorporates the features of both the Langmuir and Freundlich isotherms (Equation 7.14). This equation reduces to the Freundlich isotherm at high adsorbate concentration and the Langmuir isotherm when the constant $g$ approaches unity (Allen et al., 2004).

\[
q_e = \frac{AC_e}{1 + BC_e^g}
\]  

(7.14)

Where, $A =$ Redlich-Peterson isotherm constant ($\text{l/g}$); $B =$ Redlich-Peterson isotherm constant ($\text{l/mg}$); $g =$ Redlich-Peterson model exponent (Dimensionless)

Although linear transformations are not possible from three parameter isotherms, by taking the natural log of both sides a pseudo-linear equation is obtained (Equation 7.15).

\[
\ln(A\left(\frac{C_e}{q_e}\right) - 1) = g \ln(C_e) + \ln(B)
\]  

(7.15)

The Redlich-Peterson isotherm parameters $A$, $B$ and $g$ can then be evaluated using a systematic trial and error optimisation method. For these studies, a general procedure was applied using regression analysis from (Microsoft™ Excel) and a selection of $A$ values obtained from the biosorption literature to maximise the $R^2$ from the linear regression of a plot of $\ln[A(C_e/q_e) - 1]$ vs $\ln(C_e)$. 

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7.4.4 Isotherms error analysis

Linear regression is commonly used to establish isotherm model constants and parameters. However, the transformation of non-linear isotherm equations to linear forms can introduce systematic estimation errors (Ng et al., 2002; Vijayaraghavan et al., 2006; Kumar and Sivanesan, 2006). Therefore, apart from the correlation coefficients ($R^2$ values), the non-linear Chi-square statistic test ($\chi^2$) was used to assess the validity of the isotherm models selected (Ho, 2005).

For these studies, the Chi-square test represents the sum of the squares of differences between the experimental metal uptakes ($q_{\text{experimental}}$ mg/g) and those calculated from the isotherm models ($q_{\text{model}}$ mg/g), with each squared difference divided by the $q_{\text{model}}$ values. If the values obtained from the models and experimental data are in good agreement, the Chi-square test results should produce small numbers ($< 1$) and if significantly different they will be larger numbers ($> 1$).

The equivalent mathematical expression is given by equation 7.16.

$$\chi^2 = \sum \frac{(q_{\text{experimental}} - q_{\text{model}})^2}{q_{\text{model}}} \quad (7.16)$$
7.5. RESULTS AND DISCUSSION

7.5.1 Sorption kinetics

The uptake of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC were determined as a function of contact time and the summary plots are shown in Figure 7.2.

The uptake of all the metals follows two distinct steps, a rapid initial uptake (30-240 minutes), followed by a more prolonged period (240-1440 minutes) and approach towards equilibrium (Figure 7.2). The times to reach a pseudo equilibrium were 720, 120, 360 and 720 minutes for Cu(II) Hg(II), Pb(II) and Zn(II) with uptakes ($q_e$) of 23.4 10.5, 39.7 and 18.5 mg/g respectively. Based on these studies, a contact time of 1440 minutes was used for all subsequent studies to ensure sufficient time for the MMC-metal systems to attain equilibrium.

The uptake of metals by porous sorbents generally follows four consecutive steps (Findon et al., 1993).

Figure 7.2: Sorption kinetic profiles for Cu(II), Hg(II), Pb(II) and Zn(II) by MMC. $C_i = 100$ mg/L, $V = 100$ ml, $T = 21 ^\circ C \pm 2 ^\circ C$, 0.25 grams MMC, particle size 250-800 µm, agitation rate 350 rpm.
1. Mass transfer to boundary film layer surrounding sorbent particles (mass transfer).

2. Transport over the boundary layer to surface metal binding sites (film diffusion).

3. Transfer from external surfaces to internal binding sites (intra-particle diffusion).

4. Interactions with intra-particular binding sites (adsorption or micro-precipitation).

One or more of these steps can control the rate and amount of metal removed. If one step is much slower than the others at the same initial conditions of reaction, this is referred to as rate limiting. Steps 1 and 2 are generally very fast in well-agitated systems, while steps 3 and 4 are often reported to be rate-limiting (Guibal et al., 1995).

The relatively rapid initial uptakes observed in Figure 7.2, suggests effective mass transfer of metals and adsorption to surface binding sites (e.g. steps 1 and 2). While the more prolonged section (240-1440 minutes), may be attributed to rate limiting diffusion processes (e.g. steps 3 and 4). Similar removal trends were observed by Guibal et al. (1994), Jose et al. (1996), Sag and Aktay (2002) using chitin, chitosan, and seaweed for the biosorption of Cu(II), Cr(VI), Pb(II) and Zn(II). These authors proposed that ion-exchange and surface sorption reactions (e.g. physical and chemical sorption) with mildly acidic functional groups (e.g. carboxyl, hydroxyl, and amines) were responsible for the rapid removal. While Evans et al. (2002) and Vijayaraghavan et al. (2006) using crab shells for the biosorption of Cu(II) and Cd(II) suggested that diffusion processes (e.g. film and intra-particle diffusion) were rate controlling steps.

The following sections aim to evaluate the sorption kinetics of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC and establish if any rate limiting processes are taking place.
7.5.2 First-order kinetics

Experimental sorption data was evaluated using the linear form of the Lagergren first-order rate equation (Equation 7.3). Summary plots for Cu(II), Hg(II), Pb(II) and Zn(II) are shown in Figure 7.3 and the corresponding line equations and correlation coefficients listed in Table 7.1.

![Graphs showing first-order linear plots for Cu(II), Hg(II), Pb(II), and Zn(II).](image)

**Figure 7.3:** Summary plots of Lagergren pseudo-first-order linear equation for (a) Cu(II), (b) Hg(II), (c) Pb(II) and (d) Zn(II). Symbols = experimental data from (Figure 7.2), dashed lines = linear trend lines from (Equation 7.3). C_0 = 100 mg/L, 0.25 grams, 250-800 µm, T = 21 °C ± 2 °C.

The Lagergren pseudo-first-order linear equation failed to predict reliable sorption kinetics for Cu(II), Hg(II), Pb(II) and Zn(II) by MMC (Table 7.1). The main disadvantage of this model was it did not provide linear plots over the whole range of contact time and was generally only applicable for the first 20-60 minutes of the sorption process (Figure...
Furthermore, for this model to be valid, the intercepts of linear plots should be equal to $\ln(q_e)$ and the predicted metal uptakes from the model $q_{(\text{mod})}$ close to experimental values $q_{(\text{exp})}$ (Ho and McKay, 1998). Clearly this was not the case (Table 7.1). Therefore, the pseudo-first-order model was considered to be inappropriate and the sorption kinetics of metals by MMC is not a first-order reaction.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Linear regressions</th>
<th>$q_{e \ (\text{exp})}$</th>
<th>$q_{e \ (\text{mod})}$</th>
<th>$\ln(q_e)$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>$Y = -0.0009x + 0.7921$</td>
<td>23.4</td>
<td>1.12</td>
<td>1.3672</td>
<td>0.87</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>$Y = -0.0009x + 0.0661$</td>
<td>10.5</td>
<td>-61.35</td>
<td>1.0198</td>
<td>0.26</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>$Y = -0.0008x + 0.5937$</td>
<td>40.2</td>
<td>1.68</td>
<td>1.5985</td>
<td>0.34</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>$Y = -0.0016x + 0.9455$</td>
<td>18.5</td>
<td>1.06</td>
<td>1.2541</td>
<td>0.98</td>
</tr>
</tbody>
</table>

**Notes:** $q_{e \ (\text{exp})} =$ experimental values and $q_{e \ (\text{mod})} =$ model values

McKay et al. (1999) proposed that a possible reason for failure of the Lagergren pseudo-first order model was due to boundary layer resistance at the beginning of the sorption process. While Sharma and Bhattacharyya (2005) suggested the model was not appropriate because the equation parameter $k_1 \ (q_e - q_t)$ does not account for the total number of available metal binding sites. This model has been applied successfully to predict the metal sorption kinetics for a large range of organic and inorganic sorbents Ho and McKay (1998). However, it has also been unsatisfactory for a variety of other biosorbents tested (Reddad et al., 2002; Benaissa and Benguella, 2002; Taty-Costodes et al., 2003; Senthilkumar et al., 2006).
7.5.3 Pseudo-second-order kinetics

The pseudo-second-order kinetic model is often applied if the first-order model fails, as it generally predicts sorption over the whole range of contact times. This model is based on the capacity of the solid phase and that chemical biosorption processes are rate determining (Ho and MacKay, 1998). Experimental sorption data was evaluated using Equation 7.6. Summary plots are shown in Figure 7.4, the rate constants, experimental and predicted metal uptakes and correlation coefficients are listed in Table 7.3.

![Figure 7.4: Summary plots of pseudo-second-order linear equation for Cu(II), Hg(II), Pb(II) and Zn(II). Symbols = experimental data from (Figure 7.2), dashed line = best fit linear trend lines. C₁ = 100 mg/L, V = 100 ml, T = 21 °C ± 2 °C, 0.25 grams MMC, 250-800 µm.](image)

All plots are linear over the whole range of contact time with high R² values and the uptakes predicted from the model qₑ(mod) are in good agreement with experimental qₑ(exp) (Figure 7.4 and Table 7.2). The high R² values also indicate the validity of the pseudo-second-order model and that chemical biosorption processes are rate limiting steps (Ho and Mackay, 1998). These results are consistent with many other studies using a large range of biosorbents and commercial adsorbents for sorption of metals (Ho, 2006).
Table 7.2: Pseudo-second-order linear equation constants and correlation coefficients

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pseudo-second order kinetic model (Equation 7.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{exp}}$ (mg/g)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>23.4</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>10.5</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>40.2</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>18.5</td>
</tr>
</tbody>
</table>

The sorption rates followed the order Hg(II) > Pb(II) > Cu(II) > Zn(II) with 14.6, 1.40, 1.34 and 1.30 mg/mg/min respectively. It is also worth emphasising the higher uptake ($k_2$) obtained for Hg(II) and initial sorption rates ($h$) for Hg(II) and Pb(II) (emboldened and italicised values in Table 7.2) with respect to Cu(II) and Zn(II). Both of these metals are persistent and highly toxic within aqueous environments even at dilute concentrations (see Chapter 1 sections 1.2.3.3 and 1.2.3.4). Therefore, MMC may offer considerable potential for the detoxification of Hg(II) and Pb(II) bearing effluents before discharge into receiving waters.

Furthermore, the metal uptake and removal rates achieved by MMC in these studies are considerably faster than those reported in the literature for many other biosorbents and the more expensive commercial adsorbents (Ho and MacKay, 1998, 1999; Inbaraj and Sulochana, 2006).
7.5.4 Intra-particle diffusion

Weber and Morris (1962) developed a model to evaluate rate controlling diffusion processes of biologically resistant pollutants from wastewater. They proposed that intra-particle diffusion can be characterised by plots of specific uptake \((q_t)\) versus the root of time \((\sqrt{t})\). If intra-particle diffusion is rate limiting, then these plots should be linear. Experimental data was used to construct plots of \(q_t\) versus \(\sqrt{t}\). Summary plots for Cu(II), Hg(II), Pb(II) and Zn(II) are shown in Figures 7.5a and b, the line equations and model constants are listed in Tables 7.3 and 7.4.

![Figure 7.5: Summary intra-particle diffusion plots for Cu(II), Hg(II), Pb(II) and Zn(II). C_i = 100 mg/L, 0.25 grams MMC, 250-800 μm, T = 21 °C ± 2 °C, 350 rpm, in Graph (a) symbols = experimental data (Figure 7.2), dashed lines = linear trend line and Graph (b) dashed lines = film diffusion and surface adsorption, solid lines = intra-particle diffusion and equilibrium.](image-url)
All plots are non-linear with low $R^2$ values (Figure 7.5a and Table 7.3). However, a closer examination reveals two distinct linear sections (Figure 7.5b). The first section (30 to 240 minutes) shows a rapid uptake of metals, while the second (remaining 1200 minutes) a slower uptake for Cu(II) and Zn(II) and no change in uptake for Hg(II) and Pb(II). This suggests two or more removal processes are occurring. In well agitated systems, the boundary film layer surrounding sorbents is greatly reduced and film diffusion and metal uptake to surface binding sites is less restricted (Findon et al., 1993; Sag and Aktay, 2000). As these studies were conducted using an agitation rate of 350 rpm, mass transfer and film diffusion were not considered to be rate-limiting (see Figure 7.6).

Table 7.3: Linear equations and correlation coefficients from Graph 7.5a.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Intra-particle diffusion (Equation 7.7)</th>
<th>Linear regressions equations</th>
<th>$R^2$</th>
<th>$k_{id}$ (mg/g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>$Y = 0.2549x + 15.07$</td>
<td>0.79</td>
<td>0.0637</td>
<td></td>
</tr>
<tr>
<td>Hg(II)</td>
<td>$Y = 0.4789x + 8.0730$</td>
<td>0.26</td>
<td>0.0250</td>
<td></td>
</tr>
<tr>
<td>Pb(II)</td>
<td>$Y = 0.1001x + 2.9739$</td>
<td>0.85</td>
<td>0.1197</td>
<td></td>
</tr>
<tr>
<td>Zn(II)</td>
<td>$Y = 1.9887x + 6.6149$</td>
<td>0.85</td>
<td>0.4971</td>
<td></td>
</tr>
</tbody>
</table>

Figure 7.6: Removal of Zn(II) with different agitation rates. (Courtesy Dr Shuguang Lu).
Although MMC particles are microporous, they have dense crystalline structures due to a large CaCO₃ content (see Chapter 5 Figures 5.2 and 3). This could be restricting intra-particle diffusion and metal uptake is confined external surfaces. Sorption rates for each metal were calculated from linear sections in Figure 7.5 b and shown in Table 7.4. The rates from the first linear section suggest rapid surface adsorption, while rates in the second sections are much slower. These results and SEM-EDAX micro-analysis (see Chapter 5 Figure 5.16) support the hypothesis made for the uptake of metals by MMC to be rate controlled by intra-particle diffusion.

Table 7.4: Linear equations and correlation coefficients derived from Graph 7.5 b.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Film diffusion and surface adsorption (Linear Eqn 1)</th>
<th>R²</th>
<th>K_ad (mg/g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>Y = 2.1152x + 0.7501</td>
<td>0.93</td>
<td>0.53</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>Y = 1.3423x + -0.0494</td>
<td>0.99</td>
<td>0.28</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Y = 3.5108x + -0.5881</td>
<td>0.99</td>
<td>0.88</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Y = 1.6210x + 0.2560</td>
<td>0.98</td>
<td>0.41</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Intra-particle diffusion and equilibrium (Linear Eqn 2)</th>
<th>R²</th>
<th>K_ad (mg/g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>Y = 0.1440x + 18.053</td>
<td>0.89</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>Y = -0.0038x + 10.527</td>
<td>0.01</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Y = 0.0175x + 38.848</td>
<td>0.21</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Y = 0.1831x + 12.1240</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Notes: K_ad = Film diffusion and surface adsorption K_ad = Intra-particle diffusion and equilibrium

These observations are consistent with those reported by Evans et al. (2002) and Merrifield et al. (2004) using crab chitosan, chitosan and chitosan gel beads for the sorption of Cu(II), Zn(II), Cd(II) and Hg(II). Another possible explanation for the slower uptake could be the large hydrated radii of metals, 1.76 and 1.81 Å for Hg(II) and Pb(II) restricting diffusion into micro pores (e.g. steric hindrance). Further SEM-EDAX analysis studies would help to confirm if intra-particle diffusion is rate limiting for the biosorption of Hg(II), Pb(II) and Zn(II) by MMC.
7.5.5 Sorption isotherms

7.5.5.1 Langmuir adsorption isotherm

The derivation of a scientifically based adsorption isotherm model was first developed by Irwin Langmuir (Langmuir, 1918) for the adsorption of gas onto glass and considers sorption as a chemical process. Although this model gives no definitive information into the sorption mechanisms, it provides a theoretical maximum uptake capacity \( q_{\text{max}} \) and enables direct comparisons between biosorbents (Volesky, 2003).

However, it is important to stress here that the Langmuir model is an ideal theoretical isotherm and is based upon the following set of assumptions:

1. Sorption takes place on homogenous surfaces until a single monolayer is formed
2. All sorption sites are uniform and there is no interaction between adsorbed species
3. Adsorbed ions or molecules are not free to move on the surface.
4. The enthalpy of adsorption or binding energies for each ion or molecule is the same.

Experimental sorption data was evaluated using two forms of the Langmuir isotherm model (linear Equations. 7.9 and 7.10). Summary plots for Cu(II), Hg(II), Pb(II) and Zn(II) are shown in Figure 7.7 and the Langmuir constants \( q_{\text{max}} \) and \( K_a \) and dimensionless separation factors \( K_r \) are listed in Table 7.5.
Figure 7.7: Summary plots of Langmuir linear equations (a) Equation 7.9 and (b) = Equation 7.10, symbols = experimental data, dashed lines = best fit linear trend lines. $C_1 = 100$ mg/L, $T = 21 \degree C \pm 2 \degree C$, 250-800 µm.

All the plots are linear with high correlation coefficients (Table 7.5). These high $R^2$ values indicate that both linear equations can provide a good representation of the sorption systems (Figure 7.7a and b). The maximum uptake capacities ($q_{max}$) and sorption affinities ($K_a$) follow the order Pb(II)>Cu(II)>Zn(II)>Hg(II) for both equations. However, the $q_{max}$ and correlation coefficients obtained using Equation 7.9 were higher (Table 7.5).
While the sorption affinities \( (K_a) \) derived from using Equation 7.10 are higher for Cu(II) and Zn(II). These results clearly demonstrate that the equilibrium uptakes and sorption affinities can differ considerably depending on the linear isotherm equation used to obtain the model constants.

**Table 7.5:** Comparison of Langmuir constants and coefficients of determination.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Langmuir linear (Equation 7.9)</th>
<th></th>
<th>Langmuir linear (Equation 7.10)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_{\text{max}} ) (mg/g)</td>
<td>( K_a )</td>
<td>( K_r )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>86.2</td>
<td>0.19</td>
<td>0.06</td>
<td>0.99</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>14.6</td>
<td>0.004</td>
<td>0.65</td>
<td>0.99</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>416.7</td>
<td>0.23</td>
<td>0.04</td>
<td>0.99</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>30.5</td>
<td>0.08</td>
<td>0.30</td>
<td>0.99</td>
</tr>
</tbody>
</table>

**Notes:** \( K_r \) = the Hall dimensionless separation factor

It is also worth noting the steep initial slopes of the Cu(II) and Pb(II) isotherms (Figure 7.8a) and values emboldened in (Table 7.5) indicating the greater affinity of MMC for these metals with respect to Hg(II) and Zn(II). The dimensionless separation factor values \( (K_r) \), obtained using Equation 7.12 range between 0.03 and 0.65 for both equations, indicating that biosorption is favourable for all the metal-MMC systems, and particularly for Hg(II).

The Langmuir constants \( q_{\text{max}} \) and \( K_a \) derived from linear equations (7.8 and 7.9) were used to construct Langmuir adsorption isotherms. Summary plots for Cu(II), Hg(II), Pb(II) and Zn(II) are presented in (Figure 7.8).
In general, the good agreement of model isotherms with experimental data suggests metal removal follows the Langmuir adsorption process (Figure 7.8a and b) and implies uptake is by monolayer coverage to homogenous surface sites. This supports conclusions made in section 7.5.4 that intra-particle diffusion is rate limiting. Metal uptakes (q\text{max}) by other biosorbents and some commercial sorbents are listed in Table 7.6 for comparison. Although direct comparison may be difficult due to varying experimental conditions, the uptakes obtained by MMC in these studies (emboldened values) are comparable or higher.
<table>
<thead>
<tr>
<th>Metal</th>
<th>Sorbent</th>
<th>( q_{\text{max}} ) (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>Tree fern</td>
<td>11.7</td>
<td>Ho, 2003</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>Seaweed (\textit{Ulva lactuca})</td>
<td>65.5</td>
<td>Lau \textit{et al.}, 2003</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>Prawn shell (\textit{Panaeus monodon})</td>
<td>16.9</td>
<td>Chu, 2002</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>Activated carbon (Norit® C Gran)</td>
<td>47.7</td>
<td>Wilson \textit{et al.}, 2005</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>Ion-exchange-resin (Duolite® GT-73)</td>
<td>24.7</td>
<td>Saha \textit{et al.}, 2000</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>MMC (\textit{Cancer pagurus})</td>
<td>86.2</td>
<td>\textit{This work}</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>Corn husks</td>
<td>8.6</td>
<td>Pimentel \textit{et al.}, 2002</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>\textit{Escherichia coli}</td>
<td>26.8</td>
<td>Deng and Wilson., 2001</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>\textit{Penicillium purpurogenum}</td>
<td>70.4</td>
<td>Say \textit{et al.}, 2003</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>Ion-exchange resin (Purolite® S-920)</td>
<td>381.1</td>
<td>Lloyd-Jones \textit{et al.}, 2004</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>Activated carbon</td>
<td>12.4</td>
<td>Namasivayam \textit{et al.}, 1993</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>MMC (\textit{Cancer pagurus})</td>
<td>14.6</td>
<td>\textit{This work}</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Alfalfa (\textit{Medicago sativa})</td>
<td>119.0</td>
<td>Gardea-Torresday \textit{et al.}, 2004</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Sawdust (\textit{Pinus sylvestris})</td>
<td>22.2</td>
<td>Taty-Costodes \textit{et al.}, 2003</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Seaweed (\textit{Ecklonia radiata})</td>
<td>282.0</td>
<td>Jose \textit{et al.}, 1996</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Activated carbon (Minotaur®)</td>
<td>255.5</td>
<td>Wilson \textit{et al.}, 2005</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Ion-exchange resin (Dowex® 50W)</td>
<td>424.7</td>
<td>Pehlivan and Altun 2006</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>MMC (\textit{Cancer pagurus})</td>
<td>416.7</td>
<td>\textit{This work}</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Moss (\textit{Fontinalis antipyretica})</td>
<td>14.7</td>
<td>Martins \textit{et al.}, 2004</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Alfalfa (\textit{Medicago sativa})</td>
<td>4.9</td>
<td>Gardea-Torresday \textit{et al.}, 2004</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Coffee residues</td>
<td>13.4</td>
<td>Boonamnuayvitaya \textit{et al.}, 2004</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Ion-exchange resin (Dowex® 50W)</td>
<td>153.6</td>
<td>Pehlivan and Altun 2006</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Activated carbon (Cenatur®)</td>
<td>19.9</td>
<td>Leyva-Ramos \textit{et al.}, 2002</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>MMC (\textit{Cancer pagurus})</td>
<td>30.5</td>
<td>\textit{This work}</td>
</tr>
</tbody>
</table>
7.5.5.2 Freundlich adsorption isotherm

Experimental data was used to construct Freundlich linear isotherms (Equation 7.13). Summary plots for Cu(II), Hg(II), Pb(II) and Zn(II) are shown in Figure 7.9 and the Freundlich constants and correlation coefficients listed in Table 7.7.

![Figure 7.9](image)

**Figure 7.9:** Summary plots of linear Freundlich equation for Cu(II), Hg(II), Pb(II) and Zn(II). C_i = 100 mg/L, 21 °C ± 2 °C, 250-800 µm, symbols = experimental data, dashed lines = linear trend line.

The Cu(II), Pb(II) and Zn(II) plots are all linear with high correlation coefficients 0.99, 0.98 and 0.99 respectively (Table 7.7). This indicates that the Freundlich isotherm is also a good model for the biosorption of Cu(II), Pb(II) and Zn(II) by MMC. However, this was not the case for Hg(II), with a correlation coefficient of 0.88 (Table 7.6). The sorption capacities, (k_f) followed the same order as the Langmuir isotherms but were much lower with 105.2, 25.5, 5.72 and 0.01 mg/g for Pb(II)>Cu(II)>Zn(II)>Hg(II) respectively. While the adsorption intensities (1/n) followed the order 3.44, 2.80, 2.90 and 0.60 for Cu(II)>Zn(II)>Pb(II)>Hg(II) respectively.
**Table 7.7:** Freundlich isotherm constants and coefficients of determination.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Freundlich linear isotherm (Equation 7.13)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>0.99</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>0.88</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>0.99</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Unlike the Langmuir model, the Freundlich model can be applied for the sorption of metals on heterogeneous surfaces as well as multilayer sorption (Wang and Quin, 2005). The large differences in sorption capacities and affinities may reflect that metal uptake is taking place on sites with different energies of adsorption. As carapace from *Cancer pagurus* contains chitin, proteins and lipids (Welinder, 1976; Lee *et al.*, 1997), MMC would provide a range of metal binding ligands (e.g. hydroxyls, carboxyls and amines).

As discussed in Chapter 4, (section 4.5.2) the extent to which metals bind with biological ligands depends on the chemistry of the metal ion and the preference to form ionic or covalent bonds (Nieboer and McBryde, 1973). According to the Pearson hard and soft metals classification system, Cu(II), Pb(II) and Zn(II) are borderline metals and form stable complexes with a variety of biological ligands (Pearson, 1963). However, Hg(II) is a class A metal and soft Lewis acid due to its high polarizibility and forms strong covalent bonds with soft Lewis bases, most notably with reduced sulphur (Nieboer and Richardson, 1980). As there is a limited number of sulphur containing functional groups available on MMC (Lee *et al.*, 1997), this may explain the low sorption capacities and affinities observed for Hg(II).
Freundlich constants \((K_f\) and \(1/n\)) derived from the linear equations were used to construct Freundlich isotherms using Equation 7.12. Summary plots for Cu(II), Hg(II), Pb(II) and Zn(II) are presented in Figure 7.10.

![Figure 7.10: Summary plots of Freundlich sorption isotherms for Cu(II), Hg(II), Pb(II) and Zn(II). \(C_I = 100\) mg/L, \(V = 100\) ml, \(T = 21^\circ C \pm 2^\circ C\), 250-800 \(\mu\)m, symbols = experimental data, dashed lines = Freundlich model.](image)

The good agreement of the Cu(II) and Hg(II) experimental data with the Freundlich model isotherm suggests that this model would be appropriate for these metals. However, there is not a good agreement for Pb(II) or Zn(II) sorption systems and the model appears to underestimate uptake at the higher concentration ranges.
7.5.5.3 Redlich-Peterson adsorption isotherm

Experimental data were evaluated with the Redlich-Peterson pseudo-linear isotherm equation (Equation 7.15). Summary plots are shown in Figure 7.11 and the isotherm constants calculated by trial and error optimisation are listed in Table 7.8.

![Figure 7.11: Summary plots of linear Redlich-Peterson isotherm equation. C<sub>i</sub> = 100 mg/L, V = 100 ml, 21 °C ± 2 °C, 250-800 µm, solid symbols = experimental data, dashed lines = linear trend line.](image)

The high correlation coefficients obtained (Table 7.8) and the good agreement of model isotherms with experimental data (Figure 7.12) indicates the suitability of Redlich-Peterson model isotherm to predict the sorption process.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Redlich-Peterson pseudo-linear Eqn. In(A*C&lt;sub&gt;e&lt;/sub&gt;/q&lt;sub&gt;e&lt;/sub&gt; -1) Vs In(C&lt;sub&gt;e&lt;/sub&gt;)</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>A</th>
<th>B</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td></td>
<td>0.99</td>
<td>111.2</td>
<td>3.57</td>
<td>0.64</td>
</tr>
<tr>
<td>Hg(II)</td>
<td></td>
<td>0.99</td>
<td>0.55</td>
<td>0.04</td>
<td>1.00</td>
</tr>
<tr>
<td>Pb(II)</td>
<td></td>
<td>0.94</td>
<td>125.0</td>
<td>0.03</td>
<td>0.85</td>
</tr>
<tr>
<td>Zn(II)</td>
<td></td>
<td>0.99</td>
<td>11.0</td>
<td>1.38</td>
<td>0.71</td>
</tr>
</tbody>
</table>
However, the good agreement with the experimental sorption data is not surprising since the isotherm equation parameters $A$, $B$ and $g$ for each metal were obtained using a systematic trail and error procedure that optimises the correlation coefficients of determination. It is also worth noting that all the values of the Redlich-Peterson isotherm exponent ($g$) are $\leq 1$. This again implies that sorption follows the Langmuir model and the uptake of metals is via surface sorption processes (see section 7.4.3).

**Figure 7.12:** Summary plots of Redlich-Peterson sorption isotherms (Equation 7.14) (a) Cu(II) and Pb(II) (b) Hg(II) and Zn(II). $C_i = 100 \text{ mg/L}$, $21 \, ^\circ \text{C} \pm 2 \, ^\circ \text{C}$, 250-800 µm. Solid symbols = experimental data, dashed lines = Redlich-Peterson model.
Summary graphs of sorption isotherm models tested in this chapter are presented in Figure 7.13 for comparison.

**Figure 7.13**: Summary of isotherm model curves and experimental data for (a) Cu(II), (b) Hg(II), (c) Pb(II) and (d) Zn(II). Symbols = experimental data, solid lines = isotherm model. Light blue = Langmuir, dark blue = Freundlich and green = Redlich-Peterson.

Examination of Figure 7.13 shows that for the models tested, the Langmuir isotherm model (light blue line) provides the best correlation with the experimental data followed by the Redlich-Peterson then the Freundlich isotherm. This is in good agreement with the uptake of metals by MMC being via surface adsorption processes and supports the SEM-EDAX micro analysis obtained for Cu(II) in previous Chapters. These results are also consistent with intra-particle diffusion being the rate limiting step for the sorption of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC.
7.5.6 Isotherm error analysis

Linear transformations of non-linear isotherms to obtain model constants can introduce systematic errors (Ho et al., 2002; Allen et al., 2004; Kumar and Sivanesan, 2006). The \textit{Chi-square} statistic test ($\chi^2$) was used along with the $R^2$ values obtained from linear regressions of non-linear model isotherm equations to test the validity of using this approach (see Section 7.4.4). The results are summarised in Table 7.9.

\textbf{Table 7.9:} Comparison of $R^2$ values from linear regressions and \textit{Chi-square} statistic test

<table>
<thead>
<tr>
<th>Metal</th>
<th>Langmuir (Eq. 7.9)</th>
<th>Langmuir (Eq. 7.10)</th>
<th>Freundlich (Eq. 7.13)</th>
<th>Redlich-Peterson (Eq. 7.15)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>$R^2$</td>
<td>$\chi^2$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>7.3$^8$</td>
<td>0.99</td>
<td>0.33</td>
<td>0.94</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>0.05</td>
<td>0.99</td>
<td>1.00</td>
<td>0.99</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>8.4$^9$</td>
<td>0.99</td>
<td>3.9$^{-22}$</td>
<td>0.95</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.99</td>
<td>0.94</td>
<td>0.99</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Among the two-parameter isotherm models tested, high correlation coefficients and low \textit{Chi-square} values were observed for both forms of the Langmuir linear isotherm equations (Table 7.9). This is particularly evident for Cu(II), Hg(II) and Pb(II) and indicates the suitability of using linear transformations of the non-linear Langmuir isotherm model to predict equilibrium uptakes for these metals. The Freundlich model in general provides a good correlation and was the least appropriate for Hg(II). As expected the three-parameter Redlich-Peterson provided the highest correlation coefficients for Cu(II), Hg(II) and Zn(II) and the lowest \textit{Chi-square} values for Pb(II) and Zn(II) (Table 7.9).
7.5.7 Ion-Exchange model

The uptake of metals by various biosorbents has been extensively studied Volesky (1990), Veglio and Beolchini (1997), Forster and Wase (1997), Varma et al. (2004) and Singh et al. (2006). However, the specific removal mechanisms involved have not yet been clearly established or understood (Volesky, 2003). Several authors have suggested that the application of appropriate chemical binding models can help to elucidate these mechanisms (Sag and Aktay, 2000; Dzul-Eroza et al., 2001; Chu, 2002). Ion-exchange is frequently proposed as the main metal removal mechanism involved with seaweeds and micro-organisms (Crist et al., 1981; Avery and Tobin, 1993; Schiewer and Volesky, 1995, Da-Costa et al., 2001; Davis et al., 2003).

In these studies, the contribution of ion-exchange was considered by following the release of Na⁺, K⁺, Ca²⁺, and Mg²⁺ from MMC (main exchangeable cations) during the uptake of Cu²⁺, Hg²⁺, Pb²⁺ and Zn²⁺ using the method proposed by Sciban and Klasnja (2004). In summary, the net release-exchange of ions from each metal-MMC combination is represented by the difference between the Na(I), K(I), Ca(II), and Mg(II) concentrations after agitation with the metal solutions to that of controls (MMC and no metals). If ion-exchange is the main removal mechanism, then the ratio of metal ions adsorbed by MMC to those released (R_{a/r}) should be close to unity. This is represented mathematically by Equation 7.17, Sciban and Klasnja (2004). Where, Meⁿ⁺ = Cu²⁺, Hg²⁺, Pb²⁺ or Zn²⁺.

Results from these studies are presented in Table 7.10.

\[
R_{a/r} = \frac{\frac{[\text{Me}^{n+}]}{2}}{\frac{[\text{Na}^+] + [\text{K}^+]}{2} + [\text{Ca}^{2+}] + [\text{Mg}^{2+}]} 
\]  

(7.17)
**Table 7.10:** Cations released from MMC during sorption of Cu$^{2+}$, Hg$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$

<table>
<thead>
<tr>
<th>Metals</th>
<th>Metal uptake (meq/g)</th>
<th>Net amount ions released (meq/g)$^a$</th>
<th>$\text{R}_{a/r}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\text{Na}^+$</td>
<td>$\text{K}^+$</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>0.193</td>
<td>0.329</td>
<td>-0.004</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>0.024</td>
<td>0.012</td>
<td>-0.003</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>0.059</td>
<td>0.002</td>
<td>$2.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.143</td>
<td>0.016</td>
<td>$-2.5 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

**Notes:** $^a$Cations released during metal sorption minus ions released from controls.

The $\text{R}_{a/r}$ values show that the sum of ions released from MMC was greater than the amount of metals bound (Table 7.10). A mass balance calculation for exchanges between $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ and the test metals (taking the ion charges and contribution of $\text{H}^+$ into account) was performed to quantify the contribution of ion-exchange in the biosorption process. This revealed that ion-exchange made varying contributions towards the biosorption of Cu$^{2+}$, Hg$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ by MMC with 37.0, 10.3, 63.2 and 71.2 % respectively (Table 7.10).

Therefore, ion-exchange was not the only removal mechanism operating and other processes are involved (e.g. physical and chemical sorption and precipitation). Similar observations were reported by Ad-costa *et al.*, (2001) and Sciban and Klasnja, (2004) using brown seaweed and wood barks for the removal of Cu$^{2+}$ and Zn$^{2+}$ from aqueous solutions. While a study by (Fiol *et al.*, 2006) using olive stone wastes for the biosorption of Cd$^{2+}$, Cu$^{2+}$, Pb$^{2+}$ and Ni$^{2+}$ observed the largest ion-exchange contribution was observed for Ni$^{2+}$. 
7.6. CONCLUSIONS

The sorption rates and equilibrium uptakes of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC were evaluated using three kinetic and three adsorption isotherm models. The validity of linear transformations of non-linear isotherms to obtain model constants was assessed with the *Chi-square* statistic test. An ion-exchange model was applied to establish the contribution of ion-exchange to overall metal removal by MMC. A number of conclusions were made and these are summarised below:

1. The first-order kinetic model failed to predict sorption rates ($R^2 = 0.26-0.98$) while the pseudo-second order model provided reliable rates ($R^2 > 0.99$), with 1.34, 14.6, 1.40 and 1.30 mg/mg/min for Cu(II), Hg(II), Pb(II) and Zn(II) respectively. The intra-particle diffusion model indicated sorption proceeds via a stepwise process, with rapid uptake to surface binding sites followed by rate limiting intra-particle diffusion.

2. The *Chi-square* statistic test confirmed the validity of using linear regressions to obtain model constants and the two-parameter Langmuir model was the most appropriate for these studies.

3. Reliable uptakes were predicted using the Langmuir model ($R^2 > 0.99$), with 86.2, 14.6, 416.7 and 30.5 mg/g/MMC for Cu(II), Hg(II), Pb(II) and Zn(II) respectively. The good fit of experimental data with the Langmuir model and SEM-EDAX micro analysis confirmed metal uptake is predominantly via surface sorption processes.

4. Ion-exchanges with K$^+$, Na$^+$, Ca$^{2+}$ and Mg$^{2+}$ made varying contributions to the overall removal of metals with pH controlled (4.3-4.7) was 37.0, 10.0, 63.0 and 71.0 % for Cu$^{2+}$, Hg$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ respectively. (See Figure 7.14).
These studies have demonstrated that the sorption rates and equilibrium uptake of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC can be predicted with confidence using the pseudo-second-order and Langmuir adsorption isotherm models. The sorption process was rapid with most metal removal occurring in 60 minutes. However, due to the high mineral content of MMC, intra-particle diffusion was rate limiting. The sorption rates, especially for Hg(II), and metal uptake by MMC compared well with those of more expensive commercial adsorbents.

Both of these factors combined with the low processing costs of MMC (Chapter 5 Table 5.1) further indicate the viability of MMC as a low cost metal biosorbent. Although, these results are encouraging and go a long way towards meeting the main objectives of this thesis, a number of questions have emerged. These are listed below.
1. Would basic pre-treatments improve the metal removal efficiencies of biosorbent materials? (Chapters 4 and 5)

2. As all these studies were conducted using single metal solutions, how does MMC perform as a biosorbent in the presence of other metals-ions? (e.g. competing ion effects in multi metal solutions)

3. Is it possible to recover sorbed metals from MMC allowing for multiple sorption-desorption cycles?

To conclude this thesis, additional investigations were conducted to provide preliminary answers to these questions and identify any further work required to firmly establish MMC as viable metal biosorbent. The results from these studies are presented and discussed in Chapter 8.
8. CHAPTER 8 PRE-TREATMENTS, COMPETING IONS AND CU(II) RECOVERY
In Chapter 7, 3 kinetic models, 3 adsorption isotherm models and an ion-exchange model were used to quantify the sorption rates, equilibrium uptakes and contribution of ion-exchange during biosorption of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC. The sorption of metals follows a second order reaction and proceeds in a stepwise process, with rapid surface adsorption/precipitation followed by rate limiting intra-particle diffusion. Maximum metal uptakes were predicted with confidence using the Langmuir model. Ion-exchange made various contributions to overall removal depending on the metal. To conclude this thesis, Chapter 8 presents results from additional investigations to assess the effects of basic pre-treatments, competing ions and desorption characteristics of Cu(II) from MMC.

8.1. INTRODUCTION

8.1.1 Pre-treatments

Pre-treatments and chemical modifications have been shown to improve the metal sorption capacity of biosorbent materials (Wase and Forster, 1997). In general, pre-treatments add or remove cellular ions and molecules or expose additional metal binding sites. For example, Gloaguen and Morvan, (1997) reported that pre-treatments of wood barks by nitric acid and formaldehyde could increase metal sorption and reduce the leaching of soluble phenols and tannins. Other studies proposed that acid and alkaline rinsing of fungi, (Fourest and Roux, 1994), macro algae (Jose et al., 1999), freshwater algae (Tien, 2002) and wool fibres (Taddei et al., 2003) increased the metal sorption capacities. While, Chu (2002), Chaisuksant (2003) and Merriefield et al. (2004) reported chemical modifications of prawn shell, chitin and chitosan (e.g. mild deacetylation or encapsulation in gel beads) increased the metal uptake and specific surface areas.
Conversely, chemical treatments can have detrimental effects. For example, cross linking chitosan with gluteraldehyde to improve structural stability in acidic solutions reduced the metal sorption capacity (Guibal et al., 1995; 1999). Therefore, there is a dividing line between the effective uses of pre-treatments and chemical modifications. A suitable consideration is the cost and complexity involved e.g. acid or alkaline rinsing is easy and inexpensive (Reddad et al., 2002), while the production of chitosan from crab carapace is labour intensive, expensive and produces toxic liquid wastes (Rae and Gibb, 2003). With the above points in mind, studies were conducted to establish if acid and alkaline rinsing of *Fucus vesiculosus* could improve the Cu(II) sorption efficiency.

### 8.1.2 Competing ions

Natural water and waste effluents contain a range of dissolved and particulate matter including metals (Stumm and Morgan, 1996). Different metals or metal complexes may show a preference for specific binding sites on biosorbents, and if the affinity and chemistry of one metal is similar to another competition effects may occur (Tsezos et al., 1996; Han et al., 2006). In these studies, the effects of competing ions on sorption of metals by MMC were evaluated using single and binary solutions of Cu(II), Hg(II), Pb(II) and Zn(II) with NaCl as a background electrolyte.

### 8.1.3 Cu(II) recovery

If biosorption is to be used effectively at the industrial scale, bound metals should be able to be easily recovered in concentrated forms and the biomass regenerated and used for multiple sorption-desorption cycles (Jalali et al., 2002, Volesky et al., 2003). In the final part of this work, three typical eluting agents, HCl, H$_2$SO$_4$ and HNO$_3$ were tested to determine the potential for the desorption-recovery of Cu(II) from pre-loaded MMC.
8.2. MATERIALS

- MMC

MMC was processed as described previously and used at the 250-800µm size.

- Seaweeds

Viable and non-viable samples of *Fucus vesiculosus* were harvested from beaches and intertidal zones around the Caithness area and used at the 250-800µm particle size. Full details of processing methods are provided in Table 8.1.

8.3. EXPERIMENTAL METHODS

8.3.1 Pre-treatments

A series of batch studies were conducted to assess the uptake of Cu(II) by *Fucus vesiculosus* depending on freshness (e.g. viable or non-viable at harvest), processing and time in storage (ageing). Experimental conditions are shown in Table 8.1.

**Table 8.1:** Cu(II) sorption by *Fucus vesiculosus* with freshness, processing and ageing

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Fresh</th>
<th>Aged A</th>
<th>Aged B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact time (minutes)</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Mass (grams)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>$C_1$ (mg/L)</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>pH$_i$</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Mixing rate (rpm)</td>
<td>350</td>
<td>350</td>
<td>350</td>
</tr>
</tbody>
</table>

**Notes:** Fresh = harvested alive (viable), air dried for 24 hours, processed and used; Aged A = harvested alive, oven dried for 6 hours at 40º C, processed and stored for 2 weeks; Aged B = harvested dead (non-viable) processed and stored for 6 months before use. All studies done in triplicate (at 350 rpm) and means reported.
Pre-treatments were performed by rinsing 5-gram fractions of *Fucus vesiculosus* with 100 ml of ultra-pure water (Untreated), 0.01 mol/L HCl (H⁺ treated) or 0.01 mol/L HCl then 0.01 mol/L CaCl₂ solutions (H⁺ and Ca²⁺ treated). Full experimental conditions are given in Table 8.2. All studies done in triplicate and the means reported.

**Table 8.2**: Pre-treatments of brown seaweed *Fucus vesiculosus*

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Untreated</th>
<th>H⁺ treated</th>
<th>H⁺ and Ca²⁺ treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact time (minutes)</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Mass (grams)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>C₀ (mg/L)</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>pH₀</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Mixing rate (rpm)</td>
<td>350</td>
<td>350</td>
<td>350</td>
</tr>
</tbody>
</table>

*Notes:* Untreated = rinsed with Ultra-pure water and oven dried at 40°C for 6 hours; H⁺ treated = rinsed with 0.01 mol/L HCl and oven dried at 40°C for 6 hours; H⁺ and Ca²⁺ treated = rinsed with 0.01 mol/L HCl, oven dried at 40°C for 6 hours then rinsed with 0.01 mol/L CaCl₂ and oven dried at 40°C for 6 hours. *Fucus vesiculosus* used was harvested alive, oven dried for 6 hours at 40 ºC and aged for two weeks.

### 8.3.2 Competing ions

In the control batch, 5-gram fractions of MMC (250-800µm particle size) were contacted with 100 ml single metal solutions containing 100 mg/L of Cu(II), Hg(II), Pb(II) and Zn(II). Contact times were varied from 5-60 minutes; the pH₀ was 2 and controlled between 4.3-4.7 by the addition of 1.0 M HCl and 1.0 M NaOH. The effects of competing ion effects were evaluated by contacting 5-grams of MMC with 100 ml of binary metal solutions containing 100 mg/L of Cu(II)-Hg(II), Cu(II)-Pb(II) and Cu(II)-Zn(II) and 0.01 mol/L NaCl as a background electrolyte, 0.01 mol/L NaCl was also added to all standard solutions. Effects of ion-competition were assessed by comparing the percent metal removals from single and binary metal solutions. All studies in triplicate and means reported.
8.3.3 Cu(II) recovery

The recovery of Cu(II) from MMC was assessed using various concentrations of HCl, H$_2$SO$_4$ and HNO$_3$ as eluting agents (see Table 8.3). Five gram fractions of pre-loaded MMC (9.9 mg/g) were agitated (at 350 rpm) with 100 ml of each eluant for a period of 20 minutes. The solutions were then vacuum filtered and the particles gently rinsed with deionised water. The Cu(II) concentrations in the filtrate was determined by AAS and the metal uptake (mg/g/MMC) using the mass balance equation outlined in chapter 2 (see equation 2.4).

The desorption efficiency calculated from the mass balance using equation 8.1. All studies done in triplicate and the mean values reported.

$$\text{Desorption efficiency} = \frac{C_f}{C_i} \times 100 \quad (8.1)$$

Where $C_i$ and $C_f$ = initial and final Cu(II) concentrations (mg/L)

<table>
<thead>
<tr>
<th>Eluant</th>
<th>0.001 M</th>
<th>0.01 M</th>
<th>0.1 M</th>
<th>0.2 M</th>
<th>0.4 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl (pH$_i$)</td>
<td>2.9</td>
<td>2.2</td>
<td>1.2</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>H$_2$SO$_4$ (pH$_i$)</td>
<td>3.4</td>
<td>2.7</td>
<td>2.2</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>HNO$_3$ (pH$_i$)</td>
<td>3.7</td>
<td>1.9</td>
<td>1.3</td>
<td>1.1</td>
<td>-</td>
</tr>
</tbody>
</table>
8.4. RESULTS AND DISCUSSION

8.4.1 Pre-treatments

Figure 8.1 shows the Cu(II) removal obtained by *Fucus vesiculosus* depending on freshness of the sample when harvested, processing methods and time ageing.

![Figure 8.1](image)

**Figure 8.1:** Effects of freshness (viable or non-viable), processing and ageing on the Cu(II) removal efficiency of *Fucus vesiculosus*. \(C_I = 500 \text{ mg/L, pH}_I = 2.8, V = 100 \text{ mL, T} = 21^\circ \text{C} \pm 1^\circ \text{C,} \ 5 \text{ g, 250-800 \mu m.}

The percent Cu(II) removals achieved by *Fucus vesiculosus* depending on the processing and ageing were 49.3, 74.5 and 67.4% for freshly harvested, aged two weeks and 6 months respectively (Figure 8.1). The best removal was obtained with samples harvested alive, oven dried for 6 hours at 40°C and aged for two weeks. Therefore, the freshness of samples and the subsequent processing methods are important considerations to obtain the optimum biosorption efficiency.
Based on the results from the previous study, *Fucus vesiculosus* collected fresh, oven dried for 6 hours and aged for two weeks was selected for these studies. The Cu(II) removal efficiencies after pre-treatments of ultra-pure water, acid (HCl) and alkaline (CaCl$_2$) rinsing are shown in Figure 8.2.

![Figure 8.2](image)

**Figure 8.2:** The effects of rinsing with ultra-pure water, acid (HCl) and alkaline (CaCl$_2$) on the Cu(II) removal by *Fucus vesiculosus*. $C_i= 500$ mg/L, 5 g, 250-800µm, pH$_i = 2.8$, $T = 21^\circ C \pm 1^\circ C$, $V = 100$ mL, agitation rate 350 rpm.

The percent Cu(II) removals achieved were 74.5, 90.6 and 97.0 % for ultra-pure water, HCl and HCl and CaCl$_2$ rinsed respectively. These results and the previous study clearly demonstrate that the removal efficiency of Cu(II) by *Fucus vesiculosus* can be enhanced by 25.0-30.0 % with careful collection, processing and acid and alkaline rinsing. These pre-treatments are easy to perform, relatively inexpensive and are well worth considering for any further studies with *Fucus vesiculosus* or other species of seaweeds.
8.4.2 Competing ions

The effects of competing ions on the biosorption of metals by MMC were assessed using single and binary metal solutions of Cu(II), Hg(II), Pb(II) and Zn(II) with NaCl as a background electrolyte. The results are shown in Figures 8.3, 8.4 and 8.5.

Figure 8.3: Effects of Hg(II) on Cu(II) sorption (a) and (b) effects of Cu(II) on Hg(II) $C_1 = 100$ mg/L, pH$_f$ = 2.0, $V = 100$ mL, $T = 21 \, ^\circ C \pm 1 \, ^\circ C$, 5 g MMC, agitation rate 350 rpm.

Figure 8.3a shows that when Hg(II), is in solution with Cu(II) there was a slight increase in the Cu(II) removal (~8.0%) indicating there were no competition effects. Conversely, when Cu(II), is in solution with Hg(II) there was a 20-40% decrease in Hg(II) removal (Figure 8.3b). This suggests that Cu(II) has a higher affinity for MMC and is preferentially adsorbed, consequently exerting a competing ion effect on Hg(II).
When Pb(II) is in solution with Cu(II) a small increase (~8.0%) in Cu(II) removal was observed in the first 10 minutes (Figure 8.4a). Thereafter, removal is about the same as in single solutions, indicating that Pb(II) exerts a negligible competition effect on Cu(II) sorption. However, it appears that Pb(II) may start competing with Cu(II) for similar binding sites at contact times in excess of than 20 minutes.

![Figure 8.4: Effects of Pb(II) on Cu(II) sorption (a) and (b) Cu(II) on Pb(II) by MMC. C₁ = 100 mg/L, pH₁ = 2.0, V = 100 mL, T = 21 °C ± 1 °C, 5 g MMC, agitation rate 350 rpm.](image)

When Cu(II) is in solution with Pb(II) removal of Pb(II) is reduced by 5.0-8.0 % over the entire 60 minutes (Figure 8.4b). This suggests that Cu(II) is preferentially adsorbed by MMC and exerts a small competition effect on the sorption of Pb(II).
When Zn(II) is in solution, Cu(II) removal is reduced by 10-20% in the first 20 minutes indicating that Zn(II) competes for similar binding sites (Figure 8.5a). Thereafter, Cu(II) removal increases with time to that of single solution (~96.0 %) by 60 minutes.

![Figure 8.5: Effects of Zn(II) on Cu(II) sorption (a) and (b) Cu(II) on Zn(II) sorption by MMC C<sub>i</sub> = 100 mg/L, pH<sub>i</sub> = 2.0, V = 100 mL, T = 21 °C ± 1 °C, 5 g MMC, 350 rpm](image)

When Cu(II) is in solution, removal of Zn(II) decreased by ~ 23.0 % in the first 5 minutes, then increased to that of the single solution by 60 minutes (Figure 8.5b). These studies indicate the biosorption of metals by MMC can either be enhanced or suppressed in multi-metal solutions depending on the metals present. Further studies are required with equi-molar concentrations to fully characterise the effects of ion-competition.
8.4.3 Cu(II) recovery

Recovery of Cu(II) from pre-loaded MMC samples (9.9 mg/g) was assessed using various concentrations of hydrochloric acid (HCl), sulphuric acid (H₂SO₄) and nitric acid (HNO₃) as eluting agents. The results are shown in Figure 8.6.

![Graphs showing Cu(II) recovery vs. acid concentration](image-url)

**Figure 8.6:** Recovery of Cu(II) from MMC using (a) HCl, (b) H₂SO₄ and (c) HNO₃ as eluting agents. Contact time 20 minutes, V = 100 mL, T = 21 °C ± 1 °C, 5 g MMC, mixing rate 350 rpm.

The recovery of Cu(II) was ineffective for all the eluting agents at dilute concentrations. The best recoveries obtained were 77.7, 66.0 and 27.0% for 0.4 mol/L HCl, 0.2 mol/L H₂SO₄ and 0.2 mol/L HNO₃ respectively (Figures 8.6a, b and c). This suggest that the Cu(II) could be bound by strong chemical bonds (e.g. irreversible covalent bonding with nitrogen in amine functional groups).
To determine Cu(II) recovery over time, another study was conducted 0.2 mol/L HCl and varying contact times from 5 to 60 minutes. The results are shown in Figure 8.7.

![Graph showing Cu(II) recovery and pH evolution](image)

**Figure 8.7:** The effects of contact time on Cu(II) recovery and evolution of pH. 0.2 mol/L HCl, Cu(II) 9.90 mg/g MMC, pH$_i$ = 1.0, V = 100 mL, T = 21 °C ± 1 °C, 5 g MMC, agitation rate 350 rpm.

Figure 8.7 shows the highest recovery of Cu(II) was obtained by 5 minutes (57.7 %), then decreased to 9.2 % at 60 minutes. This shows that the recovery of Cu(II) would be fast if eluant concentration and pH are optimised. Conversely, the solution pH increases with time from 1 to 5.6 at 60 minutes due to dissolution of CaCO$_3$. As the pH increases above 2, desorption would be quickly followed by re-adsorption or precipitation when pH >5 (See Chapter 6 Figure 6.8).

Another study was conducted with 0.1 mol/L of HCl and H$_2$SO$_4$ with pH controlled to ~2.0 (Results not shown). The Cu(II) recovery increased from 6.5 and 18.0 % to 39.3 and 57.4% for HCl and H$_2$SO$_4$ respectively. To establish if complete recovery was possible a study was performed with concentrated HCl 2.0 mol/L (Results not shown). Only 36.0 % recovery was achieved and the MMC mass was reduced to 0.88 g. Clearly it would not be practical to use HCl at this concentration.
8.5. CONCLUSIONS

To conclude this thesis, additional investigations were conducted to determine the effects of basic pre-treatments on *Fucus vesiculosus*, effects of competing ions on the biosorption of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC and if recovery of Cu(II) from MMC was possible using HCl, H$_2$SO$_4$ and HNO$_3$ as eluting agents. The conclusions are summarised below.

- **Pre-treatments**

  Effective Cu(II) removal by *Fucus vesiculosus* is dependant on the freshness of samples, processing methods and time in storage. The best results were obtained from freshly harvested, oven dried for 6 hours and aged two weeks. Cu(II) sorption by *Fucus vesiculosus* can be increased by ~30.0% with simple HCl and CaCl$_2$ rinsing.

- **Competing ions**

  Metal ions either have a beneficial or detrimental effect on the biosorption of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC. Cu(II) and Pb(II) are preferentially adsorbed by MMC and compete with Hg(II) and Zn(II) for metal binding sites in binary solutions. Cu(II) and Pb(II) have small competition effect on each other in binary solutions. Further studies with multi-metal solutions at equi-molar concentrations would provide a clearer understanding of competing ion effects.

- **Cu(II) recovery**

  Effective recovery was not obtained with eluting agents HCl, H$_2$SO$_4$ and HNO$_3$ and suggests that metal uptake is by strong covalent bonding. Further studies with alternative eluting agents may improve the Cu(II) recovery.
9. CHAPTER 9 CONCLUSIONS AND FUTURE STUDIES
9.1. SUMMARY AND CONCLUSIONS

Natural materials, brown seaweed (*Fucus vesiculosus*), peat, Douglas fir wood bark (*Psudotsuga meniesii*), and two preparations of crab carapace (MMC and CMC) were evaluated as biosorbents for the removal of metals from aqueous solutions. Physical and chemical characterisation revealed that all materials were highly porous, with varying degrees of hydrophilic properties, BET surface areas and chemical functionality (*Chapter 3*). These characteristics offered potential for development as metal biosorbents.

Preliminary screening studies indicated that all materials showed potential for the rapid removal and retention of Cu(II) from the 100-1000 mg/L range and one representative of industrial wastewater (*Chapter 4 Part A*). However, the degradation of materials during mechanical agitation, leaching of soluble alginates, phenols and tannins from seaweed and wood bark caused problems with filtration and metal analysis. The hydration and swelling properties of *Fucus vesiculosus* prohibited effective use in laboratory scale column studies due to back pressure and hydrodynamic flow restrictions. MMC and CMC derived from the carapace of the *Cancer pagurus* were more durable in dynamic batch studies and stable in acidic solutions.

The less expensive MMC was selected for extended biosorption studies with a range of environmentally relevant metals (*Chapter 4 Part B*). MMC was highly efficient for the uptake and retention of Cu(II), Cd(II), Hg(II), Pb(II) and Zn(II) over the 1-1000 mg/L range and the removal of Cu(II), Hg(II), Pb(II) and Zn(II) from dilute concentrations 1-50 mg/L. MMC was also suitable for the removal of K(I), Na(I), Ca(II), Mg(II), Cd(II), Cu(II), Hg(II), Pb(II) and Zn(II) in column studies. The order of uptake correlates with the class of metal and the covalent index value of the metals (*Chapters 4 and 7*).
Based on results from (Chapter 4), the assessment of MMC and CMC was extended by inter-comparison with commercial chitin (derived from *Cancer pagurus*) and its deacetylated derivative crab chitosan for the removal of Cu(II) (Chapter 5). MMC and CMC compared favourably with the most efficient chitinous material (crab chitosan) and were more efficient for the removal of Cu(II) from acidic solutions. Furthermore, due to their high content of CaCO₃ they provided an alkaline buffering capacity and considered to be suitable for detoxification and neutralisation of highly acidic metal bearing effluents (e.g. acid mine drainage or Cu(II) etching fluids).

The assessment of MMC and MMC was extended further by another inter-comparison study with commercial metal sorbents Darco® and Norit® granular activated carbons and Dowex® 50 W ion-exchange resin beads (Chapter 6). The uptake of Cu(II) by MMC and CMC was highly efficient removing up to 99.0 % from the 1-4000 mg/L range and pH range (1 to 7). This compared favourably with the most efficient commercial sorbents, Norit® activated carbon and Dowex® ion-exchange resin.

MMC and CMC were more effective for the removal of Cu(II) at dilute concentrations in acidic solutions. Darco® activated carbon was the least efficient commercial sorbent at the experimental conditions used. The removal of Cu(II) by MMC and CMC was highly dependant on solution pH, initial concentration, particle size and mass loading. The best uptake was obtained in the pH range 4–6, using 2 grams MMC per litre at the 250-800µm particle size.

Sorption kinetics and adsorption equilibrium modelling studies demonstrated that the uptake of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC was rapid and follows the typical Langmuir adsorption process with monolayer coverage to homogenous surface binding sites (Chapter 7).
The Lagergren pseudo first order kinetic model was unreliable to predict the sorption rates ($R^2$ 0.26-0.98). While sorption rates were predicted with confidence ($R^2 > 0.99$) using a pseudo-second order model and followed the order 14.6, 1.40, 1.34 and 1.30 mg/mg/min for Hg(II)>Pb(II)>Cu(II)>Zn(II) respectively. Maximum metal uptake capacities of MMC were predicted well with the Langmuir adsorption isotherm ($R^2 = 0.99$) and followed the order of 416.7, 82.2, 30.5 and 14.6 mg/g/MMC for Pb(II)>Cu(II)>Zn(II)>Hg(II) respectively.

An intra-particle diffusion model and SEM-EDAX micro-analysis revealed that the sorption of Cu(II), Hg(II), Pb(II) and Zn(II) proceeds in two distinct steps with rapid adsorption to surface binding sites followed by a rate limiting intra-particle diffusion. Ion-exchanges with Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ was shown to have varying contributions to the overall metal removal by MMC, with 37.0, 10.0, 63.0 and 71.0 % for Cu(II), Hg(II), Pb(II) and Zn(II) respectively.

The freshness, processing methods and age of the brown seaweed *Fucus vesiculosus* was shown to have a significant effect on the Cu(II) removal efficiency. The best results were obtained from samples freshly harvested, oven dried at 40 °C for 6 hours and aged for two weeks (Chapter 8). Simple pre-treatments of *Fucus vesiculosus* by acid and alkaline rinsing increased the Cu(II) uptake by ~30.0 %. Competing ions studies with single and binary metal solutions showed that the presence of Hg(II) and Zn(II) had a detrimental effect on the sorption of Cu(II) by MMC. Small scale desorption studies indicated that the effective recovery of Cu(II) from MMC was not possible using HCl, H$_2$SO$_4$ and HNO$_3$ as the eluting agents. This suggested that Cu(II) uptake was by chemical sorption with strong covalent bonding to metal binding ligands.
This study showed that abundant natural materials brown seaweed (Fucus vesiculosus), Douglas fir wood bark (Psudotsuga meniesii) and crab carapace (Cancer pagurus) can perform as biosorbents for the removal of Cu(II) from aqueous solutions. However, crab carapace, a shellfish processing waste is easily processed into more durable granular forms and is applicable for the removal of metals in both batch adsorption and columns. The uptake of Cu(II), Hg(II), Pb(II) and Zn(II) by MMC is rapid and compares favourably with more expensive commercial sorbents.

SEM-EDAX micro-analysis, kinetic models, adsorption isotherms and ion exchange models showed that the biosorption of metals is a complex process and proceeds via physical and chemical sorption, micro-precipitation, ion exchange and intraparticle-diffusion depending on the solution chemistry, the metal and material conditioning. The major mechanisms involved in the removal of Cu(II) by MMC are summarised in Figure 9.1.

Figure 9.1: Proposed Cu(II) removal mechanisms for MMC

The alkaline nature of carapace provides a pH buffering capacity and makes it suitable for neutralisation and detoxification of highly acidic metal bearing effluents. Although the cryogenically milled carapace was marginally more efficient under some conditions, MMC is less labour intensive and more cost effective to produce. Therefore, crab carapace offers significant potential for development as viable metal biosorbent.
9.2. RECOMMENDATIONS FOR FURTHER STUDIES

This research demonstrated the potential of seaweed, wood bark and MMC as metal biosorbents and provided an insight to the sorption mechanisms operating. However, to establish the materials as viable metal biosorbents a number of questions remain unanswered.

- MMC was effective for the removal of Cu(II), Hg(II), Pb(II) and Zn(II) at dilute concentrations. Further studies may indicate the potential of MMC for the recovery of other environmentally relevant metals and pollutants e.g. radionuclides, arsenic and chromate complexes, pesticides and pharmaceuticals.

- Preliminary studies indicated that Cu(II) and Pb(II) can be effectively removed by MMC even in the presence of Hg(II) and Zn(II). Further studies are required to confirm MMC biosorption in multi-metal solutions equi-molar concentrations?

- Intra-particle diffusion was shown to be rate limiting and attributed to the large CaCO₃ content of MMC. Would acid rinsing pre-treatments improve metal uptake and accessibility to intra-particle binding sites? SEM-EDAX micro-analysis would confirm the success of such treatments. Also, acid rinsing may protonate functional groups and facilitate uptake of anionic metal complexes such as As, Au and Cr.

- Larger scale column studies are required to determine if MMC can be used to effectively treat industrial effluents e.g. acid mine drainage? Also, there is a need to design and test small scale pilot plants for the removal of Cd(II), Hg(II) and Pb(II) from industrial wastes (e.g. recovery of cadmium from batteries).
• Desorption studies using HCl, H₂SO₄ and HNO₃ as eluants revealed it was not possible to recover Cu(II) effectively from MMC. While this offers potential for immobilisation of toxic metals, recovery may be increased using alternative eluants such as CaCl₂? Also is recovery of Hg(II), Pb(II) and Zn(II) from MMC possible?

• Although wood bark and seaweed showed potential for biosorption of Cu(II), leaching of soluble alginates and organics and swelling of Fucus vesiculosus restricted use. Pre-treatments with formaldehyde or encapsulation in a stable matrix (e.g. alginate beads) may reduce leaching and facilitate use in column studies Gloaguen and Morvan (1997) and Papageorgiou et al. (2007).

• If metal recovery is not possible, there is the safe disposal or recycling of metal laden materials to consider. Can metal enriched MMC be incinerated to recover toxic metals in concentrated amounts and disposed of to restricted landfill sites?

• A possible use for Cu(II) laden carapace may be as a soil amendment for nutrient deficient agricultural soils or a buffer to neutralise acidic soils Anon, (2003). Although crab carapace is not a natural fungicide or nematocide, it has high chitin content and promotes growth of chitin eating bacteria Speigel et al., (1986). The exoskeletons of fungi and harmful varieties of nematode eggs are rich in chitin. Therefore, chitin added to soil creates a hostile environment by feeding bacteria that eats them Anon, (2000). Also chitin stimulates soil organisms to secrete enzymes called chitinases that degrade flea egg shells, Eco Diagnostics, (2006).

If appropriate funding can be sourced to develop some of these studies, the utilisation of crab carapace may bring added value to an often problematic waste.
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APPENDICES
## APPENDIX A

**Table 1.1a** Solubility limits for sodium hydroxide precipitation (Source: Rorrer, 1998)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Metal hydroxide</th>
<th>Theoretical solubility limits</th>
<th>Practical treatment limits</th>
</tr>
</thead>
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<td></td>
<td>Precipitate (mg/L)</td>
<td>pH</td>
<td>Precipitate (mg/L)</td>
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<tr>
<td>Cr$^{3+}$</td>
<td>Cr(OH)$_3$</td>
<td>0.02</td>
<td>7.0</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>Cu(OH)$_2$</td>
<td>0.0002</td>
<td>8.5</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>Ni(OH)$_2$</td>
<td>0.001</td>
<td>10.3</td>
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<tr>
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<td>Zn(OH)$_2$</td>
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<td>9.0</td>
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<td>Pb$^{2+}$</td>
<td>Pb(OH)$_2$</td>
<td>7.0</td>
<td>9.2</td>
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<tr>
<td>Cd$^{2+}$</td>
<td>Cd(OH)$_2$</td>
<td>0.002</td>
<td>11.2</td>
</tr>
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<td>Material</td>
<td>Country</td>
<td>Metal</td>
<td>Reference</td>
</tr>
<tr>
<td>---------------------------</td>
<td>---------</td>
<td>----------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Algal biomass</td>
<td>U.K</td>
<td>Pb$^{2+}$</td>
<td>Malik <em>et al</em>., 2002</td>
</tr>
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<td>Almond shells</td>
<td>USA</td>
<td>Cu$^{2+}$</td>
<td>Toles <em>et al</em>., 2002</td>
</tr>
<tr>
<td>Apricot stones</td>
<td>Turkey</td>
<td>Cu$^{2+}$, Pb$^{2+}$</td>
<td>Beker <em>et al</em>., 2003</td>
</tr>
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<td>Aquatic plants</td>
<td>India</td>
<td>Cu$^{2+}$, Pb$^{2+}$</td>
<td>Shekinah <em>et al</em>., 2002</td>
</tr>
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<td>Blast furnace slag</td>
<td>India</td>
<td>Cu$^{2+}$, Ni$^{2+}$</td>
<td>Gupta, 1998</td>
</tr>
<tr>
<td>Bone charcoal</td>
<td>U.K.</td>
<td>Cu$^{2+}$, Pb$^{2+}$</td>
<td>Lewis, 1995</td>
</tr>
<tr>
<td>Coal</td>
<td>U.K.</td>
<td>Cr$^{3+}$, Cr$^{6+}$</td>
<td>Laktos <em>et al</em>., 2002</td>
</tr>
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<td>Coffee beans</td>
<td>China</td>
<td>Cu$^{2+}$, Cd$^{2+}$</td>
<td>Minamisawa <em>et al</em>., 2005</td>
</tr>
<tr>
<td>Coconut pith</td>
<td>Pakistan</td>
<td>Cd$^{2+}$, Cr$^{6+}$</td>
<td>Kadirvelu and Namasivayam, 2003</td>
</tr>
<tr>
<td>Coir pith</td>
<td>India</td>
<td>Hg$^{2+}$, Cr$^{6+}$, Ni$^{2+}$</td>
<td>Namasivayam and Sangeetha, 2006</td>
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<tr>
<td>Fly ashes</td>
<td>India</td>
<td>Cu$^{2+}$, Zn$^{2+}$</td>
<td>Gupta <em>et al</em>., 1998</td>
</tr>
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<td>Hazelnut shells</td>
<td>Greece</td>
<td>Ni$^{2+}$</td>
<td>Demirbas <em>et al</em>., 2002</td>
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<td>Lignite</td>
<td>UK</td>
<td>Cd$^{2+}$, Cu$^{2+}$, Hg$^{2+}$</td>
<td>Allen and Brown, 1995</td>
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<td><em>Moringa oleifera</em></td>
<td>Pakistan</td>
<td>Pb$^{2+}$</td>
<td>Nadeen <em>et al</em>., 2007</td>
</tr>
<tr>
<td>Nut hulls</td>
<td>India</td>
<td>Cd$^{2+}$, Cu$^{2+}$</td>
<td>Madhava-Rao <em>et al</em>., 2006</td>
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<tr>
<td>Olive stones</td>
<td>Italy</td>
<td>Cu$^{2+}$, Cr$^{6+}$, Pb$^{2+}$</td>
<td>Paganelli <em>et al</em>., 1991</td>
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<td>Peanut shells</td>
<td>Portugal</td>
<td>Cd$^{2+}$, Cu$^{2+}$</td>
<td>Volpe <em>et al</em>., 2003</td>
</tr>
<tr>
<td>Peat</td>
<td>USA</td>
<td>Cr$^{3+}$, Cr$^{6+}$</td>
<td>Mohan and Pittman, 2006</td>
</tr>
<tr>
<td>Petroleum coke</td>
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<td>Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$</td>
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<td>Seed husks</td>
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<td>Spent tyres</td>
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<td>Cd$^{2+}$, Cr$^{3+}$, Cu$^{2+}$</td>
<td>Sollars <em>et al</em>., 2001</td>
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<td>Straw</td>
<td>India</td>
<td>Cd$^{2+}$</td>
<td>Kannang and Rengasamy, 2005</td>
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<td>Waste ashes</td>
<td>China</td>
<td>Cd$^{2+}$, Hg$^{2+}$</td>
<td>Zhang and Itoh, 2002</td>
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**Notes:** References from this table not included in the main references are listed below.


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Table 1.3a Selection of commercial cation exchange resins (Holl et al., 2002)

<table>
<thead>
<tr>
<th>Product</th>
<th>Manufacturer</th>
<th>Support</th>
<th>Functionality</th>
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</thead>
<tbody>
<tr>
<td>Dowex 50 W</td>
<td>Dow</td>
<td>Divinyl-benzene</td>
<td>Sulphonate</td>
</tr>
<tr>
<td>Duolite A7</td>
<td>Rohm and Haas</td>
<td>Phenol-formaldehyde</td>
<td>Secondary amine</td>
</tr>
<tr>
<td>Duolite A 365</td>
<td>Rohm and Haas</td>
<td>Polystyrene</td>
<td>Tertiary amine</td>
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<tr>
<td>Amberlite IRA 67</td>
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<td>Purolite A 830</td>
<td>Purolite</td>
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<td>Purolite A 830</td>
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<td>Secondary amine</td>
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<td>Purolite A 830</td>
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<td>Fuji PEI CS</td>
<td>Fuji Comp</td>
<td>Chitosan</td>
<td>Secondary amine</td>
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Table 1.4a A global review of materials evaluated as biosorbents for the removal of metal from aqueous solutions

Due to the size of this table and the associated references that are not included in the main thesis references. The interested reader is directed to the CD-ROM provided at the back of the thesis.
### APPENDIX B

#### Table 2.1a Atomic Adsorption Spectrophotometer operational conditions applied for metal analysis

<table>
<thead>
<tr>
<th>Metal</th>
<th>Flame</th>
<th>Lamp</th>
<th>Lamp current (ma)</th>
<th>Wavelength (nm)</th>
<th>Slit width (µm)</th>
<th>Band pass (nm)</th>
<th>LWR (mg/L)</th>
<th>LOD (mg/L)</th>
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**Notes:** LOD = Limit of detection; LWR = Linear working range; ma = milli-amps; nm = nano-metres; (10⁻⁹) µm = micro metres; (10⁻⁶). Instrument calibrations were conducted twice daily.
APPENDIX C
Figure 1.1a: SEM-EDAX elemental spectra for Mechanically Milled Carapce
Figure 1.2a: SEM-EDAX elemental spectra for Cryogenically Milled Carapace
Figure 1.3a: SEM-EDAX elemental spectra for DARCO® activated carbon
Figure 1.4a SEM-EDAX elemental spectra for NORIT® activated carbon
Figure 1.5a: SEM-EDAX elemental spectra for DOWEX® W 50 ion-exchange resin
APPENDIX D

The publications listed below and more other scientific outputs associated with this PhD thesis are provided in the attached CD-ROM.

Peer reviewed manuscripts:


Conference Presentations:

December 2003 (Platform presentation) 4th European Meeting on Environmental Chemistry (EMEC 4) Plymouth, U.K. Title: Crab carapace: A low-cost biosorbent for the removal of toxic metals from aqueous solutions

December 2003 (Poster presentation) 4th European Meeting on Environmental Chemistry (EMEC 4) Plymouth, U.K. Title: Copper removal from aqueous solutions using biosorbent materials: Sorption kinetics and adsorption equilibrium isotherm comparisons

December 2003 (Platform presentation) UHI Millennium Institute Post Graduate Research Conference, Lews Castle, Isle of Stornoway, UK Title: Crab carapace a viable biosorbent for the removal of Cu(II), Hg(II), Pb(II) and Zn(II)

December 2002 (Poster presentation) 3rd European Meeting of Environmental Chemistry (EMEC 3) Geneva, Switzerland Title: Natural and commercial sorbents for the removal of copper from aqueous media

April 2002 (Platform presentation) 3rd IWA Young Researchers Conference, University of Nottingham, U.K. Title: Crab Carapace: A low cost biosorbent for the removal of copper from aqueous solutions.

April 2002 (Poster presentation) 3rd International Water Association (IWA) World Water Congress, Melbourne, Australia Title: Removal of metals from aqueous wastes using natural Chitinious materials

February 2002 (Platform presentation) UHI Millennium Institute Post Graduate Research Conference, Sabhal Mòr Ostaig, Isle of Skye, UK Title: The Use of Natural Products for The Purification of Potable Water and The Treatment of Wastewater

December 2002 (Poster presentation) 3rd European Meeting of Environmental Chemistry (EMEC 3) Geneva, Switzerland Title: Natural and commercial sorbents for the removal of copper from aqueous media