

A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media

E.L. Cochrane^{a,*}, S. Lu^{a,b}, S.W. Gibb^a, I. Villaescusa^c

^a Environmental Research Institute, The North Highland College, UHI Millennium Institute, Castle Street, Thurso, Caithness, KW14 7JD Scotland, United Kingdom

^b Resources and Environmental Engineering Institute, East China University of Science and Technology, No.130, Mei Long Road, Xu Hui District, Shanghai 200237, China

^c Departament d'Enginyeria Química, Universitat de Girona, Campus de Montilivi, Avda Lluís Santaló s/n, 17071 Girona, Spain

Received 13 September 2005; received in revised form 20 January 2006; accepted 26 January 2006

Available online 13 March 2006

Abstract

Three biosorbents, crab carapace, the macroalgae *Fucus vesiculosus* and peat were compared with two commercial materials, an activated-carbon and an ion-exchange resin for the removal of copper from aqueous media. Kinetic models of Lagergren first-order, pseudo-second order and intraparticle diffusion were used to model the data. The process for all materials is best represented by the pseudo-second order rate model. Langmuir and Freundlich isotherms were used to describe the sorption equilibrium data. Maximum uptake values were 79.4, 114.9 and 71.4 mg g⁻¹ for crab carapace, *F. vesiculosus* and ion-exchange resin, respectively. Langmuir and Freundlich isotherm models could not be fitted to the experimental data for peat and activated-carbon. Ion-exchange was calculated to contribute ~75%, 77% and 44% to the total biosorption by crab carapace, *F. vesiculosus* and peat, respectively. The removal efficiencies of crab carapace and *F. vesiculosus* were >95% and comparable with those achieved using ion-exchange resin. Results from this study suggest that both crab carapace and *F. vesiculosus* are efficient and effective biosorbent materials for the removal of copper from aqueous solutions and given that they are also low-cost, may be considered viable alternatives to activated-carbon and ion-exchange resin.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Crab carapace; Macroalgae; Peat; Biosorption; Equilibrium isotherm

1. Introduction

It is well recognised that the presence of heavy metals in the aquatic environment can result in a number of problems. Most metals are rather insoluble in water with a neutral or basic pH, and rather than dissolving, they are rapidly adsorbed to particulate matter or assimilated by living organisms [1]. To prevent deteriorating surface water quality, legislation governing the levels of heavy metals, such as copper, zinc, lead and cadmium, discharged from industries is becoming progressively stricter.

Conventional methods for removing dissolved heavy metal ions from aqueous media include chemical precipitation, chemical oxidation and reduction, ion-exchange and activated-carbon adsorption [2]. However, these processes have significant dis-

advantages including incomplete metal removal; particularly at low concentrations and high operational costs. Biosorption technology, utilising natural materials or industrial and agricultural wastes to passively remove metals from aqueous media, offers an efficient and cost-effective alternative compared to traditional chemical and physical remediation and decontamination techniques [3].

There is a large volume of literature relating to the performance of different biosorbents for the removal of different heavy metals under various experimental conditions, e.g. see review by Bailey et al. [4]. Work carried out to date has shown that each biosorbent has its own individual characteristics and that the performance of each is influenced by a range of factors including pH and the presence of other ions in solution [5]. However, due to the heterogeneity of experimental and analytical procedures, evaluation criteria and the expression of the results, comparison of data from different authors is difficult. Consequently, it has been difficult to translate the advances made in the labora-

* Corresponding author. Tel.: +44 1847 889587; fax: +44 1847 890014.
E-mail address: Emma.Cochrane@thurso.uhi.ac.uk (E.L. Cochrane).

tory into industrial application and realise the potential of the biosorption process.

In addition to the performance, a number of other factors greatly influence the choice and viability of natural materials as biosorbents, for example the cost of processing materials, metal selectivity and regeneration of materials. Cost is a very important factor when considering materials for use as biosorbents. It is generally recognised that a material can be deemed 'low-cost' if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry [4].

Crab carapace, an abundant by-product of the shell-fishing industry has been proposed as a potential biosorbent with extensive studies having been carried out by Rae and Gibb [6]. Most crab meat is canned or frozen and the carapace can be obtained cheaply as a by-product or waste [2]. Crab carapace consists principally of CaCO_3 and chitin, usually cross-linked with protein and a proportion of lipids [7]. It is a highly porous material with a reported 150,000–200,000 mm^2 of pore canals permeating the cuticle of the edible crab, *Cancer pagurus* [8]. This characteristic makes it extremely viable for metal uptake from aqueous media.

Macroalgae is another abundant, potential biosorbent. It is readily available and some macroalgae have been identified for the ion-exchange properties associated with their polysaccharide content (particularly pronounced in brown algae) [4]. They also possess large quantities of biopolymers (alginates) that can bind heavy metals, therefore their metal uptake capacities are high, for example, *Sargassum* sp. showing gold uptake as high as 40% of the biomass dry weight [9].

Peat has also been recognised as potential material for water pollution control. Ho et al. [10] demonstrated the use of peat for nickel removal, however removal was found to be poor compared with other metals such as lead [11]. Peat is a complex material containing lignin and cellulose [12]. The type of peat used, the metal concentration, ionic strength and pH all have major effects on the metal removal capacity [4].

Here we compare three biosorbent materials (crab carapace, the macroalgae *Fucus vesiculosus* and peat) with two commercial materials (activated-carbon and ion-exchange resin) for the removal of copper from aqueous solutions.

2. Materials and methods

2.1. Preparation of biosorbents/sorbents

Cryogenically milled crab carapace of *C. pagurus* commonly known as the edible or brown crab, was obtained from Carafiltration Ltd. N.E. Lincs, UK. The carapace was sieved using a mechanical sieve (Retsch, AS 200 mechanical sieve) to obtain particles within the size range 250–800 μm . It was then washed several times using deionised water (Millipore Direct Q3 Water Purification System) until the water ran clear and then dried at 60 °C in a laboratory oven for 24 h.

The brown macroalgae *F. vesiculosus* was collected from Thurso Bay, Thurso, Caithness, UK. It was washed thoroughly with deionised water and then air-dried at room temperature (~20 °C for 48 h). The material was then milled and mechan-

ically sieved to give particles in the range 250–800 μm . The macroalgae particles were then washed using deionised water and dried overnight in an oven at 40 °C.

Peat was obtained from Dale and Achkeepster Farms Ltd., Causeway Mire, Caithness, UK. It was air-dried for 48 h, crudely broken using a hammer and dried in an oven for 24 h at 60 °C. It was then milled and sieved to give particles in the size range 250–800 μm .

A strongly acidic ion-exchange resin (Dowex® 50WX4 Fine Mesh, Sigma–Aldrich Chemical Company, UK) was used in all experiments. The resin was washed using deionised water and then dried at 40 °C before use.

The activated-carbon used in this study was Norit® granular activated-carbon ROW 0.8, pellets (Sigma–Aldrich Chemical Company, UK). The material was washed using deionised water and then dried at 40 °C for 24 h.

2.2. Metal solutions

Copper solutions (100 mg l^{-1}) were prepared using copper(II) sulphate (CuSO_4 , anhydrous 98%, Acros Organics). CuSO_4 was chosen as the metal salt since sulphate ions exist more widely in most wastewater or mine drainage i.e. potential application for biosorption.

Calcium, magnesium, potassium and sodium solutions, used as standards for flame photometry, were prepared using laboratory grade $\text{Ca}(\text{NO}_3)_2$, MgCl_2 , KCl and NaCl salts, respectively. All solutions, their dilutions and standards were prepared using deionised water (Millipore Direct Q3 Water Purification System). Any pH adjustments were made using 0.1 M hydrochloric acid or sodium hydroxide solutions.

2.3. Metal analysis

Flame atomic-absorption spectroscopy (FAAS, Instrumentation Laboratory Inc., Model 357) was used for the analysis of copper (Cu^{2+}) and magnesium (Mg^{2+}). Concentrations were determined after calibrating the instrument with standards within the concentration range of 0.5–10 and 0.1–1.0 mg l^{-1} for Cu^{2+} and Mg^{2+} , respectively. The light source was a hollow-cathode lamp of the element that was being measured. Flame photometry (Sherwood, Model 410) was used to analyse concentrations of dissolved sodium (Na^+), potassium (K^+) and calcium (Ca^{2+}) in solution. All working standards were prepared by diluting a stock solution containing 1000 mg l^{-1} metal ion with deionised water.

2.4. Sorption kinetics and adsorption isotherms

Batch sorption experiments were conducted at room temperature (20 ± 1 °C) on a rotary shaker (IKA® KS 260 basic) at 350 rpm, using capped bottles (Azlon® 150 ml). In the sorption kinetic experiments, 0.5 g of sorbent was thoroughly mixed with Cu^{2+} solution (100 ml; 100 mg l^{-1}) at a pH of 4.2 with no further pH control. Samples were drawn at predetermined time intervals to a maximum of 12 h. After shaking, 10 ml of the resulting mixture was filtered through Whatman® filter paper (GF/A glass

micro-fibre filter paper, 1.6 μm pore size), the final pH recorded (Jenway, Model 3205), and to all samples, 50 μl of 1 M HCl was added before being stored in a refrigerator (4 ± 1 °C). The filtrate was then analysed for metals by FAAS and flame photometry. Control experiments were conducted under the same experimental conditions using deionised water without Cu^{2+} .

The residual metal concentration was obtained by calculating the difference between the initial and final metal concentration in solution. Percentage removal of Cu^{2+} was calculated as removal (%) = $(1 - C_f/C_i) \times 100$, where C_f and C_i are the final and initial Cu^{2+} concentration in solution, respectively. Batch experiments investigating the effects of initial pH were conducted as above for a continuous 12 h. pH adjustments were made using additions of 0.1 M HCl and 0.1 M NaOH.

Batch experiments were also conducted with Cu^{2+} concentrations of 10, 20, 25, 50, 75, 100, 150, 200, 250, 300 and 400 mg l^{-1} . Samples were mixed for a continuous 24 h and the resulting filtrate analysed for its Cu^{2+} concentration.

For the adsorption isotherm experiments, sorbent (0.1–0.4 g) was added to Cu^{2+} solution (100 ml, 100 mg l^{-1} , pH 4.2). The bottles were shaken at room temperature as in the previous experiment for a continuous 12 h after which the final pH was recorded and Cu^{2+} concentration determined. Metal removal data from the equilibrium batch sorption experiments was applied to the adsorption isotherm model, according to Langmuir, which is expressed as:

$$q_e = \frac{q_{\text{max}} b C_e}{1 + b C_e} \quad (1)$$

or in its linearised form:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \quad (2)$$

where q_{max} is the maximum sorption capacity (mg g^{-1}), q_e the amount of metal ions adsorbed at equilibrium (mg g^{-1}), C_e the solute concentration at equilibrium (mg l^{-1}) and b is the equilibrium constant related to the energy of sorption which quantitatively reflects the affinity between the sorbent and sorbate [13].

Data was also applied to the isotherm model of Freundlich. The Freundlich relationship is an empirical equation based on sorption on a heterogeneous surface and assumes that different sites with several adsorption energies are involved [14,15]. It is expressed as:

$$q_e = k C_e^{1/n} \quad (3)$$

or in its linearised form:

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \quad (4)$$

where k and n are the Freundlich constants denoting the relative adsorption capacity and the intensity of adsorption, respectively.

Sequential batch studies were carried out by adding 0.5 g sorbent to Cu^{2+} solution (100 ml; 100 mg l^{-1}). The bottles were shaken at room temperature at 350 rpm for 24 h after which the resulting filtrate was analysed for its Cu^{2+} concentration. The remaining solution was discarded and fresh solution added to

the loaded sorbent. The experiment was then repeated as above for 10 days.

2.5. Kinetic modelling

Three different models were used in this study to determine the sorption kinetics of Cu^{2+} , the Lagergren first-order rate model [17], the pseudo-second order model [16] and the intraparticle diffusion model [17].

The first-order rate expression of Lagergren based on solid capacity is generally expressed as follows [17]:

$$\frac{dq_t}{dt} = k_{1,\text{ad}}(q_e - q_t) \quad (5)$$

where q_e and q_t are the amounts of metal ions adsorbed onto the material (mg g^{-1}) at equilibrium and at time t , respectively; $k_{1,\text{ad}}$ is the rate constant of first-order (min^{-1}). After integration between boundary conditions ($t=0-t$ and $q_t=0-q_e$), Eq. (5) becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_{1,\text{ad}}}{2.303} t \quad (6)$$

The pseudo-second order equation is based on the sorption capacity of the solid phase and is expressed as:

$$\frac{dq_t}{dt} = k_{2,\text{ad}}(q_e - q_t)^2 \quad (7)$$

where $k_{2,\text{ad}}$ is the rate constant of second order biosorption (mg g^{-1}), q_e the amount of metal ions adsorbed at equilibrium (mg g^{-1}) and q_t the amount of soluted sorbate on the surface of the biosorbent at any time t (mg g^{-1}) [16]. For boundary conditions ($t=0-t$ and $q_t=0-q_e$), Eq. (7) becomes Eq. (8), and is the integrated rate law for a pseudo-second order reaction [16].

$$\frac{t}{q_t} = \frac{1}{k_{2,\text{ad}} q_e^2} + \frac{1}{q_e} t \quad (8)$$

The study of the kinetics of sorption provides valuable information on the time required to reach equilibrium and is key to understanding the influence of variables on sorption. The rate of sorption is particularly important, mainly in applications as in the industrial wastewater treatment.

In this study the intraparticle diffusion model of Weber and Morris [17] is used, and is expressed as:

$$q_t = \frac{k_w}{m} t^{1/2} \quad (9)$$

where m is the mass of adsorbent (g), q_t the amount of metal ions adsorbed at time t (mg g^{-1}) and k_w is the initial rate of intraparticle diffusion ($\text{mg l}^{-1} \text{s}^{-0.5}$).

According to McKay [18], there are four stages in the adsorption process of which any one or more may control the rate at which the solute is adsorbed and the amount of solute that is adsorbed onto the solid particles. The four steps are described as: (i) solute transfer from the solution to the boundary film bordering the polymer surface, (ii) solute transport from boundary film to the sorbent surface, (iii) solute transfer from the sorbent surface to the intraparticle active sites and (iv) interactions

of the solute molecules with the available sites on the internal surface.

2.6. Surface area analysis

The specific surface area of each material, except for peat [19], was determined using the Brunauer Emmett and Teller (BET) single point method [14]. This was carried out using a Micromeritics (Flowsorb III 2305/2310) surface analyser with nitrogen gas as the adsorbate. Samples were out-gassed by passing dry nitrogen over the sample for a stated time to clean the surface of any absorbed matter e.g. water, which would affect the surface area by blocking pores.

3. Results and discussion

3.1. Equilibrium contact time

Fig. 1 shows the percentage of Cu^{2+} removed by the five materials versus contact time corresponding to an initial Cu^{2+} concentration of 100 mg l^{-1} . Both the commercial sorbents showed excellent removal of Cu^{2+} especially the ion-exchange resin, Dowex, removing almost 99% Cu^{2+} after just 1 h of contact time. However, crab carapace and the macroalgae *F. vesiculosus* showed comparable results in the initial stages of the biosorption process and even though equilibrium was not reached by the macroalgae after 12 h, almost 93% removal was achieved after 1 h contact time. This rapid uptake is in accordance with literature published, for example, Herrero et al. [20] observed that over 90% of total cadmium adsorption is achieved in the first 25 min of contact. Among several studies on biosorption kinetics of metals by seaweed biomass, it was found that the sorption rate increases sharply at the beginning of the process, followed by a slower uptake rate as equilibrium is approached [21].

Crab carapace showed equally comparable results with activated-carbon, both achieving almost 50% after 1 h contact time and a removal of 98.3% and 95.9%, respectively, after 12 h of contact time.

The adsorption by crab carapace was quite slow compared with the results of previous studies such as those described by

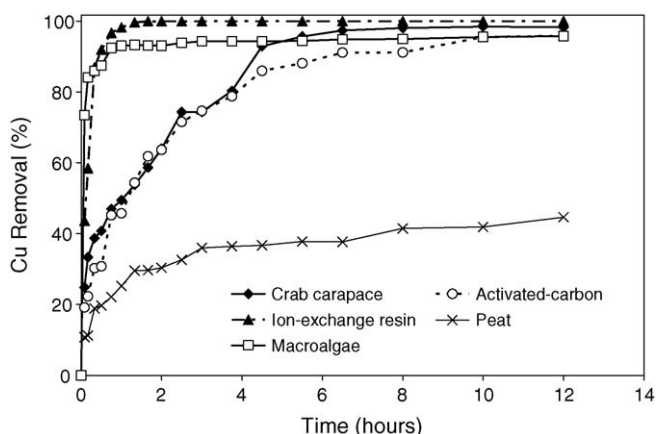


Fig. 1. Percentage removal of Cu^{2+} after 12 h contact time (particle size, $250\text{--}800 \mu\text{m}$; T , $20 \pm 1 \text{ }^\circ\text{C}$; pH, 4.2; C_i , 100 mg l^{-1} ; m , 0.5 g of sorbent).

McKay [18], as equilibrium was not reached after 12 h. Evans et al. [23] reported that chitosan-based crab carapace had a relatively high initial uptake rate, which decreased with time and may take hundreds of hours to reach equilibrium, suggesting that intraparticle diffusion may be the rate limiting step.

Peat displayed poor removal and only achieved 45% removal after 12 h contact. This is consistent with other results for peat under these conditions [11] and it is a possibility that removal would improve under different experimental conditions such as at lower Cu^{2+} concentrations. Peat is also a complex soil material and there are many types of peat due to the plant material that constitutes its formation. The type of peat as well as the pH, ionic strength and metal concentration all have an effect on sorption.

The concentrations of Ca^{2+} , Mg^{2+} , K^+ and Na^+ ions eluted after the 12 h of contact time with Cu^{2+} (100 mg l^{-1}) were also determined and the results shown in Fig. 2(a). The concentrations of these ions were used to indicate the significance of the ion-exchange mechanisms contributing to the total biosorption process. It was observed that almost 40 and 16 mg l^{-1} Ca^{2+} and Mg^{2+} , respectively, were eluted from the crab carapace after 12 h. Control studies showed that there was a smaller release of Ca^{2+} and Mg^{2+} ions from crab carapace when mixed with deionised water than when mixed with Cu^{2+} solution. These ions do not play any part in the ion-exchange process. This smaller release of ions with deionised water is clearly demonstrated in Fig. 2(b).

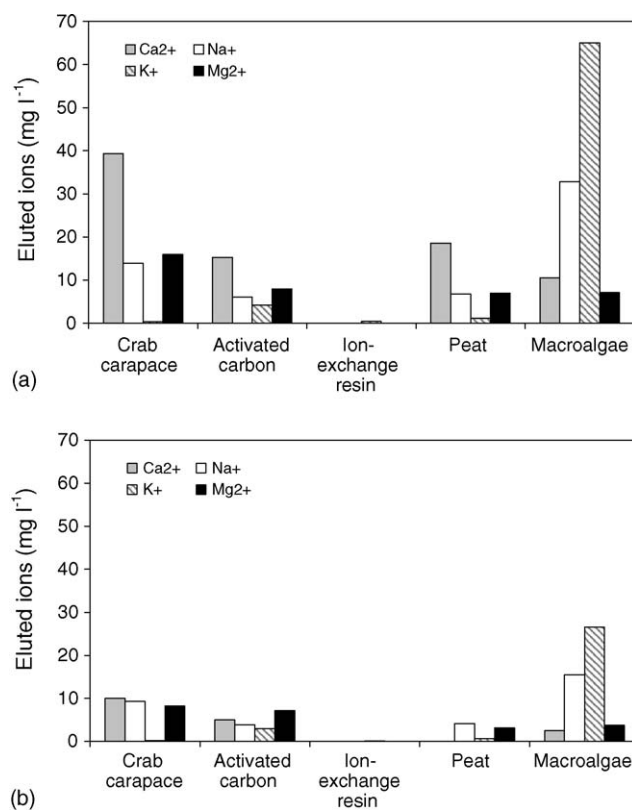


Fig. 2. Elution of Ca^{2+} , Na^+ , K^+ and Mg^{2+} ions after 12 h contact time, with: (a) Cu^{2+} (100 mg l^{-1}) and (b) 'deionised water' (particle size, $250\text{--}800 \mu\text{m}$; T , $20 \pm 1 \text{ }^\circ\text{C}$; pH, 4.2; m , 0.5 g of sorbent).

A mass balance calculation, taking into account ion charge, was performed to quantify the contribution of ion-exchange to the biosorption process. It was calculated that for crab carapace, 47%, 21%, 7% and 0.1% of the total removal by biosorption was accounted for by ion-exchange between Cu^{2+} and Ca^{2+} , Mg^{2+} , Na^+ and K^+ , respectively. For peat, 30%, 10%, 4% and 0.4% of the total biosorption was accounted for by ion-exchange with Ca^{2+} , Mg^{2+} , Na^+ and K^+ , respectively, whilst for the macroalgae, ion-exchange was calculated to contribute 77% with 13%, 9%, 24% and 31% accounting for Ca^{2+} , Mg^{2+} , Na^+ and K^+ , respectively.

The results of this study clearly demonstrate that ion-exchange is a highly significant component of the biosorption mechanism i.e. total ion-exchange accounts for 75% of total biosorption of Cu^{2+} by crab carapace, 44% of total biosorption by peat and 77% of total biosorption by the macroalgae. In addition, the relative proportions of the counter-ions released appears to be a function of the composition of the biosorbent e.g. Ca^{2+} is the dominant ion released from crab carapace, a material rich in CaCO_3 .

CaCO_3 is the main inorganic component in crab carapace where chitin is the main organic fraction [9]. The chemical groups in crab carapace are also particularly suited for sequestering anionic species. Due to the amine moieties they contain, biomass with high amounts of chitin and chitosan is specifically promising for biosorption [9]. The removal of metals using chitin and chitosan has been documented by Rae and Gibb [6] where it was shown that chitinous materials were effective biosorbent materials. The extraction of chitin or chitosan can be fairly costly; however natural biomaterials containing chitin have been recognised as effective biosorbents for metal removal.

The calculated surface area of crab carapace and other biosorbents, determined by the BET method are presented in Table 1. The highly porous structure of crab carapace may account for this relatively large surface area of $33.4 \text{ m}^2 \text{ g}^{-1}$ in comparison with other materials. However, since the active sites are distributed in the carapace non-uniformly on the microscale, it is inappropriate to characterise its sorption capacity based on the surface area [24]. Peat also has a high specific surface area ($32.5 \text{ m}^2 \text{ g}^{-1}$) and is extremely porous, two characteristics which are extremely important in biosorption [12].

Surface area is an important parameter since a larger surface area increases the number of sites available for surface sorption processes. A smaller particle size increases the surface area; this is clearly demonstrated by crab carapace where particle sizes

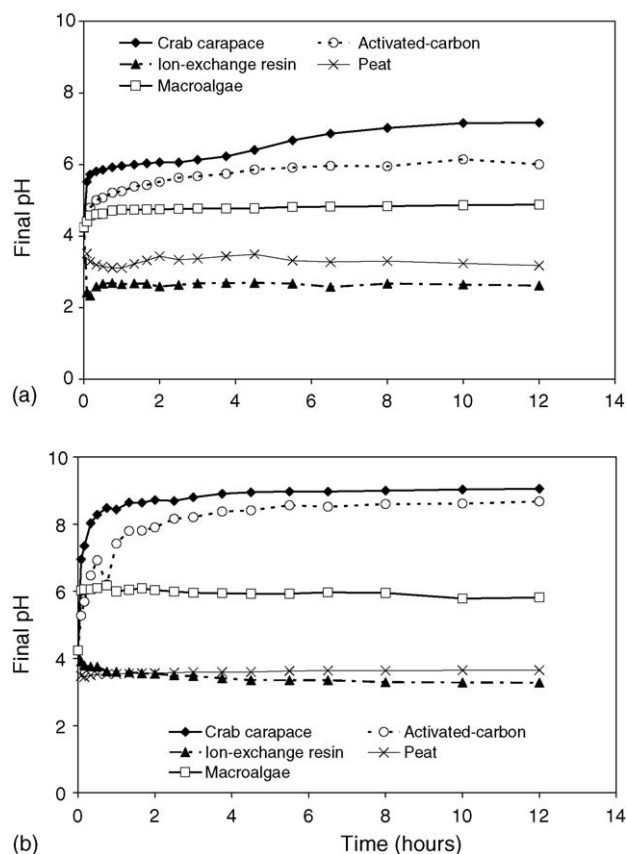


Fig. 3. Final pH of solute with sorbent in contact for 12 h with: (a) Cu^{2+} solution (100 mg l^{-1}) and (b) 'deionised water' modified to an initial pH of 4.2.

between 250–800 and 800–1500 μm give a surface area of 33.4 and $30.5 \text{ m}^2 \text{ g}^{-1}$, respectively. The effects of particle size on metal removal with crab carapace have been extensively studied and it has been shown that as particle size decreases there is a corresponding increase in metal removal [6].

3.2. Effects of pH and initial pH

The change in pH over the 12 h of contact is shown in Fig. 3 along with the results of a control study where the materials were mixed for 12 h with deionised water. There was an increase in pH from 4.2 to around 7.1, 6.0 and 4.9 in the cases of crab carapace, activated-carbon and macroalgae, respectively. For ion-exchange resin and peat the pH lowered to pH 2.6 and 3.2, respectively. This is to be expected as the ion-exchange resin

Table 1
BET surface area results for selected materials

Material description	Outgassing temperature/time	Weight loss (outgassing %)	Surface area ($\text{m}^2 \text{ g}^{-1}$)
Cryogenically milled carapace 250–800 μm	70 °C/20 h	3.05	33.4
Cryogenically milled carapace 800–1500 μm	70 °C/20 h	2.55	30.5
Cryogenically milled carapace (Cu^{2+} treated, 250–800 μm)	70 °C/20 h	4.52	22.8
Activated-carbon	60 °C/20 h	2.43	780
Ion-exchange resin	25 °C/65 h	56.0	<0.02
Macroalgae (<i>Fucus vesiculosus</i>)	70 °C/20 h	4.38	0.22
Peat [19]	N/A	N/A	32.5

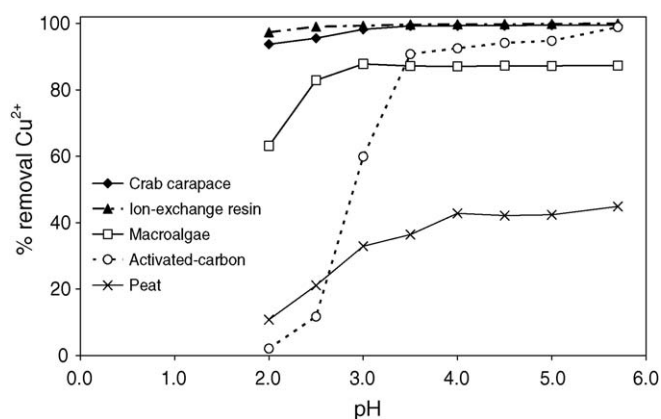


Fig. 4. Percentage removal of Cu^{2+} with different initial pH (particle size, 250–800 μm ; T , $20 \pm 1^\circ\text{C}$; C_i , 100 mg l^{-1} ; m , 0.5 g).

used in this study was a strongly acidic, hydrogen form resin. Peat is derived from partially decayed plant material and contains humic acids; therefore the low final pH for peat is consistent with proton (H^+) release due to competing Cu^{2+} ions for available sites. A rise in pH for crab carapace and *F. vesiculosus* can be explained by an ion-exchange between free Cu^{2+} in solution and Ca^{2+} or K^+ ions present in the material. This is consistent with previous data [26]. Overall, there is a lower final pH when Cu^{2+} ions are present in solution (in comparison with deionised water as shown in Fig. 3b) due to exchange of H^+ and Cu^{2+} ions.

Fig. 4 shows the percentage removal of Cu^{2+} (100 mg l^{-1} at $20 \pm 1^\circ\text{C}$) when the solution was adjusted to different initial pHs. As shown in Fig. 4 the metal removal increased with increasing pH up to around pH 4.0 and then remained fairly constant with further increases in pH.

Similar trends have been observed in studies with other materials [15,22]. It is shown in Fig. 4 that for peat and activated-carbon there was little or no metal removal at pH 2.0, this can be explained by the fact that at this low pH value the H^+ ions compete with Cu^{2+} for surface sites [22]. As the pH is increased there is a decrease of positive surface charge, which results in lower coulombic repulsion of the sorbing metal ions [13].

The rapid rise in removal efficiency from pH 2.0 to 3.0 using *F. vesiculosus* can be explained by observations described by Crist et al. [25] that zero-point charge would be found at pH 3.0 for algal biomass and that above this; algal cells would have a negative charge. At pH 3 reactions would be promoted between metal cations as there would be attractions between positively charged cations and negatively charged binding sites. Crab carapace showed removal of over 90% at all pHs tested. This was comparable with ion-exchange resin, which also gave over 90% removal across the pH range.

3.3. Effect of initial metal concentration

The metal uptake by the five materials in respect to different initial metal concentrations is shown in Fig. 5. There is a general decrease in Cu^{2+} removal with an increase in initial concentrations above 75 mg l^{-1} . Crab carapace however showed almost 100% removal for all concentrations. It is interesting to note

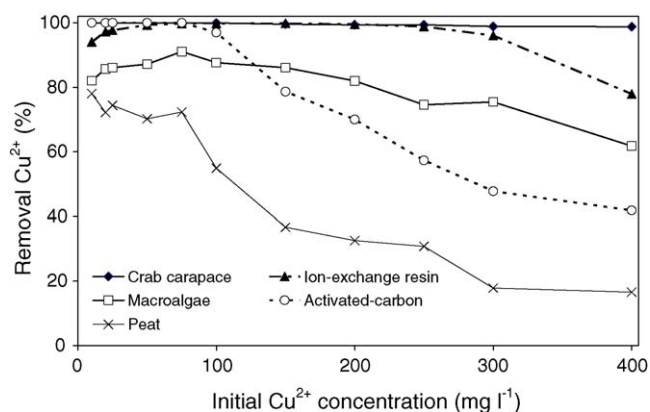


Fig. 5. Percentage removal of Cu^{2+} with different initial Cu^{2+} concentrations. Twenty-four hour contact time (particle size, 250–800 μm ; T , $20 \pm 1^\circ\text{C}$; pH, 4.2; m , 0.5 g).

that at concentrations below 100 mg l^{-1} peat removal was significantly higher than in previous experiments. This shows that equilibrium sorption capacity is highly dependent on the initial metal concentration.

3.4. Sorption isotherms

The Langmuir and Freundlich adsorption isotherms of Cu^{2+} are shown in Fig. 6. The isotherms for peat and activated-carbon are not shown due to the inability to fit the isotherms equations (Eqs. (2) and (4)) to the experimental data for these materials. In other studies using peat it has been possible to fit data to both isotherm equations [11], it is possible that the inability to fit the adsorption isotherm of peat and activated-carbon was due to or affected by the slight change in the Cu^{2+} removal from solution even at a pH greater than 4.

It was observed that both the Langmuir and Freundlich isotherm models fit the experimental data for crab carapace, *F. vesiculosus* and ion-exchange resin very well with calculated maximum uptake capacities of 79.4, 114.9 and 71.4 $\text{mg Cu}^{2+} \text{g}^{-1}$ respectively. The q_{max} values (calculated by fitting the Langmuir isotherm model to the experimental data) are very important in considering the suitability of materials for biosorption as they give an indication of the total number of binding sites that are available [14]. The maximum uptake values from this study are presented and compared with other materials in Table 2. A higher value of b for ion-exchange resin and crab carapace indicates a higher affinity of the sorbent towards Cu^{2+} than *F. vesiculosus*. The uptake capacities of crab carapace and macroalgae are low compared to results obtained using another species of carapace (*Portunus sanguinolentus*) [26]. However, they are quite high in comparison to many other biomasses studied, for example in the study of biosorption of copper by waste sugar beat pulp authors achieved a maximum uptake of 28.5 mg g^{-1} [27].

The Langmuir isotherm model however makes a number of assumptions such as monolayer-based sorption. It also assumes that all the binding sites on the sorbent are free sites, ready to accept the sorbent from solution [14]. Therefore ion-exchange

Table 2
Langmuir and Freundlich isotherm constants data and maximum uptake (q_{\max}) of Cu^{2+} for selected biosorbent materials

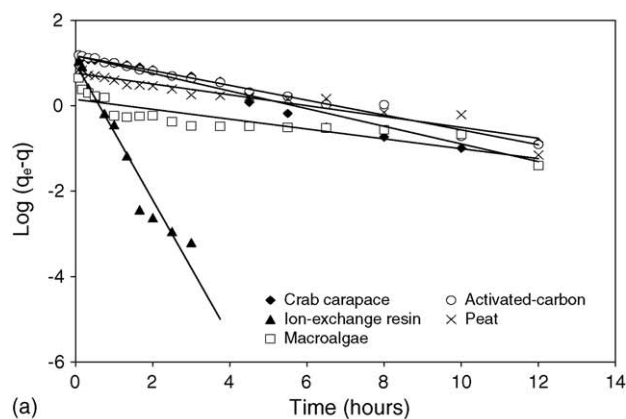
Material	q_{\max} Cu^{2+} (mg g^{-1}) (batch data)	Langmuir constant b	Freundlich constant n	Freundlich constant K_F	Reference
Crab carapace (<i>Cancer pagurus</i>)	79.4	0.621	3.05	30.4	This work
Macroalgae (<i>Fucus vesiculosus</i>)	114.9	0.049	1.654	9.09	This work
Ion-exchange resin	71.4	0.611	14.12	51.5	This work
Macroalgae (<i>Ulva lactuca</i>)	52.1	0.060		8.15	[31]
Macroalgae (<i>Turbinaria ornate</i>)	104.2	0.0028	1.41	0.787	[32]
Crab shell (<i>Portunus sanguinolentus</i>)	204.1	0.0039	2.05	6.29	[26]

is not considered in the Langmuir model so does not reflect all the mechanisms involved in this study.

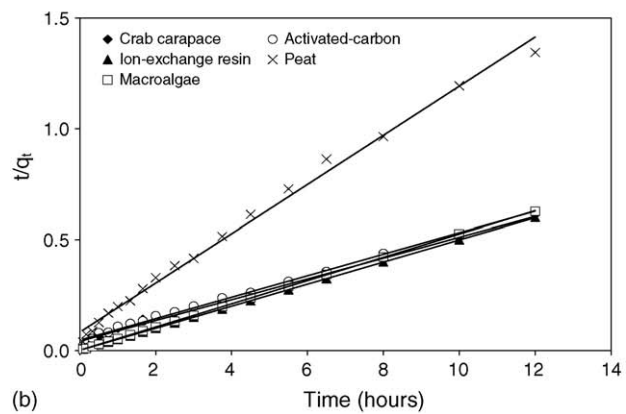
3.5. Kinetic studies and sorption dynamics

Data from the batch studies on sorption of Cu^{2+} on the five different materials were analysed using three different kinetic models to determine the time required to reach equilibrium. Data is shown in Fig. 7 together with regressions for: (a) Lagergren first-order, (b) pseudo-second order and (c) intraparticle diffusion, kinetic models.

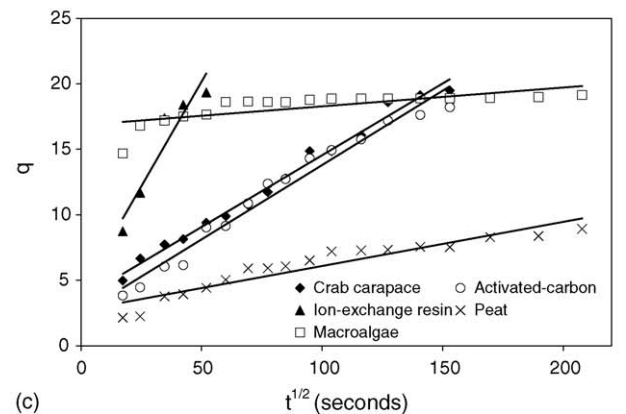
The correlation coefficients for the pseudo-second order rate equation and the other kinetic models obtained from the linear plots are listed in Table 3. In all materials, the first-order equation



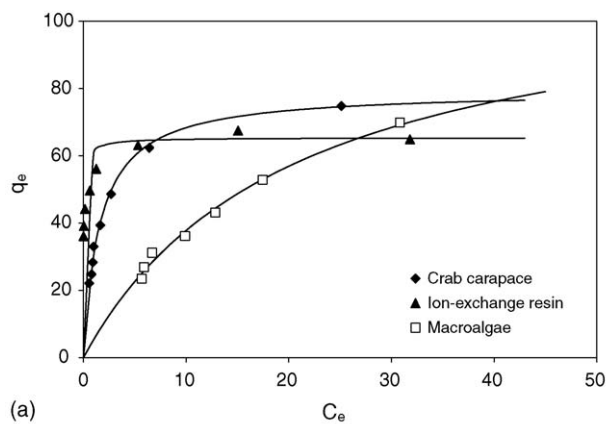
(a)



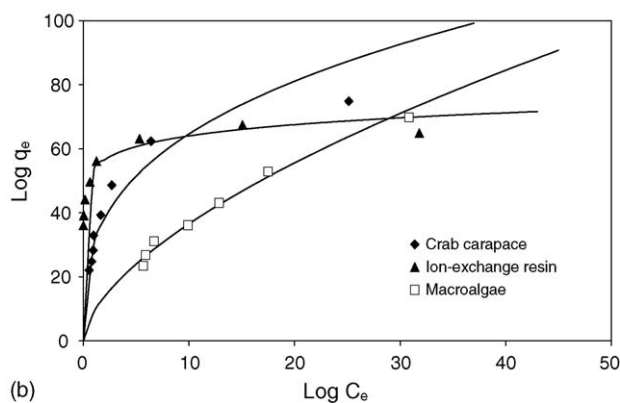
(b)



(c)



(a)



(b)

Fig. 6. Sorption isotherms of (a) Langmuir isotherm and (b) Freundlich isotherm. Twelve-hour contact time (particle size, 250–800 μm ; T , 20 ± 1 $^{\circ}\text{C}$; pH , 4.2; C_i , 100 mg l^{-1} ; m , 0.5 g of sorbent). Lines represent modelled data.

Fig. 7. Kinetic models: (a) first-order, (b) pseudo-second order and (c) intraparticle diffusion model, after 12 h contact time (particle size, 250–800 μm ; T , 20 ± 1 $^{\circ}\text{C}$; pH , 4.2; C_i , 100 mg l^{-1} ; m , 0.5 g of sorbent).

Table 3

Correlation coefficients of the kinetic models first-order (first-order), pseudo-second order (second order) and intraparticle diffusion (Int-diff) for Cu^{2+} sorption on the five materials for 100 mg l^{-1} initial Cu^{2+} concentration

	R^2 (first-order) $\frac{dq_t}{dt} = k_{1,ad}(q_e - q_t)$	R^2 (second order) $\frac{dq_t}{dt} = k_{2,ad}(q_e - q_t)^2$	R^2 (Int-diff) $q_t = \frac{k_w}{m} t^{1/2}$
Cryogenically milled carapace	0.947	0.991	0.988
Macroalgae (<i>Fucus vesiculosus</i>)	0.746	1.000	0.538
Peat	0.904	0.994	0.892
Activated-carbon	0.986	0.996	0.971
Ion-exchange resin	0.952	0.999	0.904

of Lagergren did not apply well throughout the whole range of contact times, which can be seen in Fig. 7(a). The sorption system for all materials does not therefore follow a first-order reaction. The insufficiency of the first-order model to fit the kinetic data could possibly be due to a boundary layer controlling the beginning of the sorption process [28]. This is also consistent with most cases in the literature.

The pseudo-second order model is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate [17]. The correlation coefficients are considerably lower for intraparticle diffusion compared to those of the pseudo-second order where the coefficients are all in excess of 0.99. The nature of the rate-limiting step in a batch system can be assessed from the properties of the solute and sorbent [16].

According to the equation for intraparticle diffusion by Webber and Morris, the plot for q versus $t^{1/2}$ should be linear. The experimental data for all materials does not equate to linearity therefore indicating that intraparticle diffusion is not the only mechanism involved. From Fig. 7 it is clear that intraparticle diffusion is not the sole rate-determining step and that Cu^{2+} sorption onto these biosorbent materials is best represented by a pseudo-second order rate model. This is in agreement with studies carried out on other biosorbents e.g. peat and pith [16] and other metals such as chromium(VI) [29].

3.6. Sequential batch studies

Fig. 8(a) shows the uptake (q) accumulated by each material over a 10-day cycle. Over the 10 days there was a gradual decrease in the additional copper uptake for all materials (Fig. 8(b)) and after 5 days there was no noticeable change in the accumulated uptake values for most of the materials, all of which achieved saturation. The exception being crab carapace, where after 10 days, a removal efficiency of $\sim 62\%$ and incomplete saturation was observed. It is however likely that precipitation occurred in this process as the final pH after day 1 was around pH 7.5 for crab carapace. Therefore removal cannot be accepted as solely adsorption. At this pH precipitation of Cu^{2+} at the material surface in the hydroxide or carbonate forms is thermodynamically favoured; this could be clearly seen in scanning electron microscope observations. The incomplete saturation of crab carapace in comparison with the other materials could be due to the crab carapace being 'broken' by the release of Ca^+ ions therefore providing new accessible active sites.

Isotherm models such as Langmuir suggest that this sequential loading of metal onto a sorbent is not theoretically possible. However one of the conditions for the validity of Langmuir type adsorption equilibrium is that equilibrium occurs up to the formation of a monolayer [30]. The Langmuir isotherm assumes free sites i.e. not ion-exchange; however it is well recognised that biosorption is to a large degree based on ion-exchange [14] and includes precipitation and complexation.

This multi-batch experiment could be useful in future studies for applying the biosorption mechanism in an industrial application as the reuse of the material with out the need for regeneration can be observed, keeping processing costs to a minimum. Initial desorption and regeneration studies using crab carapace (results not shown) showed that the regeneration and reuse of the material is not possible in the 'raw' untreated state. This is due to the

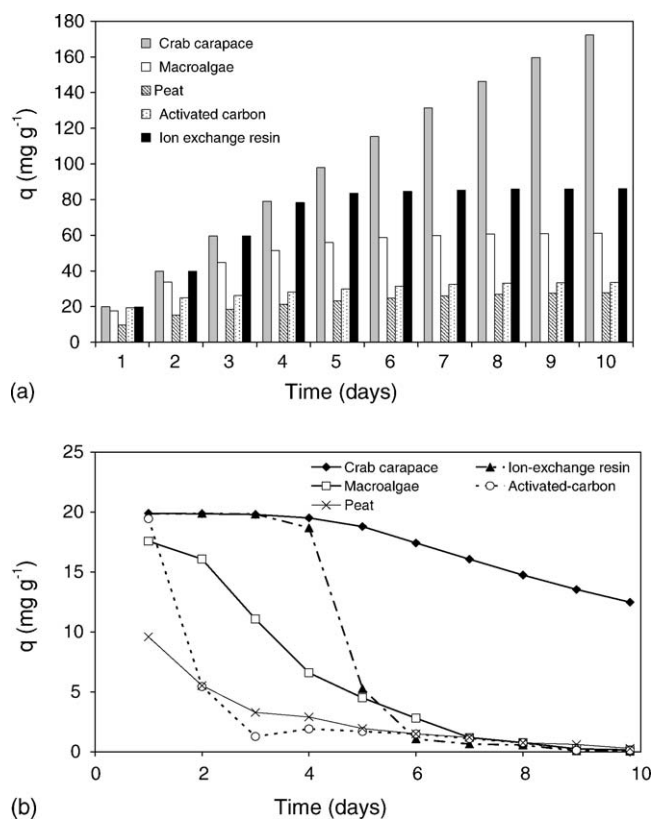


Fig. 8. The accumulated uptake: (a) and the additional uptake, (b) of Cu^{2+} over a 10-day sequential batch cycle. Twenty-four hour contact time for each batch cycle (particle size, 250–800 μm ; T , 20 ± 1 $^{\circ}\text{C}$; pH, 4.2; C_i , 100 mg l^{-1} ; m , 0.5 g of sorbent).

structure of the carapace being extensively altered during the biosorption and subsequent desorption process. Further work and more in-depth studies are required to investigate this use of crab carapace for industrial application.

4. Conclusions

The sorption process and kinetics of Cu^{2+} onto crab carapace, *F. vesiculosus*, peat, activated-carbon and ion-exchange resin have been studied. Based on these results the following conclusions have been made. It has been shown for crab carapace that a decrease in particle size corresponds to an increase in surface area and therefore an increase in available active sites, suggesting an overall increase in metal removal.

The kinetics of Cu^{2+} onto crab carapace, *F. vesiculosus* and ion-exchange resin follow a pseudo-second order rate equation. Ion-exchange was calculated to contribute approximately 75%, 77% and 44% of total biosorption by crab carapace, *F. vesiculosus* and peat respectively. The Langmuir and Freundlich isotherm equations fit the experimental data of crab carapace, *F. vesiculosus* and ion-exchange resin. Crab carapace in particular has proved to be an effective biosorbent with the possible sequential loading of metal onto the material providing an ideal basis for industrial application.

The aim of this study was to compare three biosorbent materials with two commercially available materials. It can be concluded from the three biosorbents investigated in this study, the macroalgae, *F. vesiculosus* and crab carapace are effective and efficient biosorbent materials for the removal of copper from aqueous solutions. Given that they are also low-cost materials they may be considered viable alternatives to activated-carbon and ion-exchange resin.

Acknowledgements

Mr. Didier Esteve is gratefully acknowledged for his assistance in the experimental work carried out in this study and Mr. Jim Marr, Department of Chemistry, University of Aberdeen for undertaking the BET surface area analysis.

References

- [1] E.A. Laws, Aquatic Pollution an Introductory Text, third ed., John Wiley and Sons, New York, 2000.
- [2] H.K. An, B.Y. Park, D.S. Kim, Crab shell for the removal of heavy metals from aqueous solutions, *Water Res.* 35 (2001) 3551–3556.
- [3] B. Volesky, Potential of biosorption, in: B. Volesky (Ed.), Sorption and Biosorption, BV Sorbex Inc., Montreal – St. Lambert, Que., Canada, 2003.
- [4] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, *Water Res.* 33 (1999) 2469–2479.
- [5] B. Volesky, Z.R. Holan, Biosorption of heavy metals, *Biotechnol. Progress* 11 (1995) 235–250.
- [6] I.B. Rae, S.W. Gibb, Removal of metals from aqueous solutions using natural chitinous materials, *Water Sci. Technol.* 47 (2003) 189–196.
- [7] M.Y. Lee, J.M. Park, J.W. Yang, Micro precipitation of lead on the surface of crab shell particles, *Process Biochem.* 32 (1997) 671–677.
- [8] T.F. Hegdahl, F. Gustavsen, J. Silness, The structure and mineralization of the carapace of the crab (*Cancer pagurus* L.), *Zool. Scripta* 6 (1977) 101–105.
- [9] B. Volesky, Sorption by biomass, in: B. Volesky (Ed.), Sorption and Biosorption, BV Sorbex Inc., Montreal – St. Lambert, Que., Canada, 2003.
- [10] Y.S. Ho, D.A.J. Wase, C.F. Forster, Batch nickel removal from aqueous solutions by sphagnum moss peat, *Water Res.* 29 (1995) 1327–1332.
- [11] Y.S. Ho, G. McKay, Batch lead(II) removal from aqueous solution by peat: equilibrium and kinetics, *Trans IChemE.* 77 (1999), part b.
- [12] D.A.J. Wase, C.F. Forster, Y.S. Ho, Low-cost biosorbents: batch processes, in: D.A.J. Wase, C.F. Forster (Eds.), Biosorbents for Metal Ions, Taylor and Francis Ltd., London, 1997.
- [13] I. Villaescusa, M. Martínez, N. Miralles, Heavy metal uptake from aqueous solution by cork and Yohimbe bark wastes, *J. Chem. Technol. Biotechnol.* 75 (2000) 810–816.
- [14] B. Volesky, Evaluation of biosorption performance, in: B. Volesky (Ed.), Sorption and Biosorption, BV Sorbex Inc., Montreal – St. Lambert, Que., Canada, 2003.
- [15] Z. Aksu, Equilibrium and kinetic modelling of cadmium(II) biosorption by *C. vulgaris* in a batch system: effect of temperature, *Sep. Pur. Technol.* 21 (2001) 285–294.
- [16] Y.S. Ho, G. McKay, Sorption of dyes and copper onto biosorbents, *Process Biochem.* 38 (2003) 1047–1061.
- [17] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*, *J. Hazard. Mater.* B105 (2003) 121–142.
- [18] G. McKay, The adsorption of basic dye onto silica from aqueous solution-solid diffusion model, *Chem. Eng. Sci.* 39 (1984) 129–138.
- [19] S.J. Allen, G. McKay, J.F. Porter, Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems, *J. Colloid Interface Sci.* 280 (2004) 322–333.
- [20] R. Herrero, B. Cordero, P. Lodeiro, C. Rey-Castro, M.E. Sastre de Vicente, Interactions of Cadmium(II) and protons with dead biomass of marine algae *Fucus* sp., *Mar. Chem.* 99 (2006) 106–116.
- [21] P. Lodeiro, J.L. Barriada, R. Herrero, M.E. Sastre de Vicente, The marine macroalga *Cystoseira baccata* as biosorbent for cadmium(II) and lead(II) removal: kinetic and equilibrium studies, *Environ. Pollut.* 142 (2006) 264–273.
- [22] I. Villaescusa, N. Fiol, M. Martínez, N. Miralles, J. Poch, J. Serarols, Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, *Water Res.* 38 (2004) 992–1002.
- [23] J.R. Evans, W.G. Davids, J.D. MacRae, A. Amirbahman, Kinetics of cadmium uptake by chitosan-based crab shells, *Water Res.* 36 (2002) 3219–3226.
- [24] H. Niu, B. Volesky, Characteristics of anionic metal species biosorption with waste crab shells, *Hydrometallurgy* 71 (2003) 209–215.
- [25] R.H. Crist, K. Oberholser, N. Shank, M. Nguyen, Nature of bonding between metallic-ions and algal cell-walls, *Environ. Sci. Technol.* 15 (1981) 1212–1217.
- [26] K. Vijayaraghavan, K. Palanivelu, M. Velan, Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles, *Bioresour. Technol.* 97 (2006) 1411–1419.
- [27] Z. Aksu, I. Alper İšoğlu, Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, *Process Biochem.* 40 (2005) 3031–3044.
- [28] G. McKay, Y.S. Ho, J.C.Y. Hg, Biosorption of copper from wastewaters: a review, *Sep. Purif. Methods* 28 (1999) 87–125.
- [29] N. Fiol, J. Poch, I. Villaescusa, Chromium (VI) uptake by grape stalks wastes encapsulated in calcium alginate beads: equilibrium and kinetic studies, *Chem. Speciation Bioavail.* 16 (2004) 25–33.
- [30] W. Stumm, J.J. Morgan, Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters, third ed., John Wiley and Sons, New York, 1996.
- [31] T.C. Lau, P.O. Ang, P.K. Wong, Development of seaweed biomass as a biosorbent for metal ions, *Water Sci. Technol.* 47 (2003) 49–54.
- [32] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Batch and column removal of copper from aqueous solution using a brown marine alga *Turbinaria ornate*, *Chem. Eng. J.* 106 (2005) 177–184.