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Effective removal of zinc ions from aqueous solutions using crab carapace biosorbent

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Abstract

The carapace of the crab (*Cancer pagurus*), a waste material disposed of by the seafood industry, has recently been shown to have potential as a biosorbent for the removal of metals from aqueous media. Crab carapace in the particle size ranges 0.25–0.8 mm and 0.8–1.5 mm were used to investigate the effects of agitation speed, contact time, metal concentration and initial pH on the removal of Zn^{2+}. In sequential-batch process Zn^{2+} uptakes of 105.6 and 67.6 mg/g were recorded for 0.25–0.8 mm and 0.8–1.5 mm particles, respectively, while values of 141.3 and 76.9 mg/g were recorded in fixed-bed column studies. Binary-metal studies showed that the presence of Cu^{2+} or Pb^{2+} significantly suppressed Zn^{2+} uptake. This study confirms that crab carapace may be considered a viable and cost-effective alternative to commercial activated carbon or ion-exchange resins for the removal of metals from aqueous media.

Keywords: Biosorption; Crab carapace; Zinc; Sequential-batch process; Fixed-bed column

1. Introduction

The anthropogenic emission of dissolved metals into the aquatic environment has aroused serious public concern since metals are persistent and have potential to be bioaccumulated by a range of organisms [1]. Some metals, such as copper, zinc and iron are considered bioessential while others such as cadmium, lead, mercury and chromium are highly toxic. However, even bioessential metals may cause physiological and ecological problems if present at significant concentrations [2]. One metal ion which is often released into the environment through industrial activities at concentrations of physiological and ecological concern is zinc (Zn^{2+}). In the Dangerous Substances Directive (76/464/EEC) of the European Union, zinc has been registered as List 2 Dangerous Substance with Environmental Quality Standards being set at 40 μg/L for estuaries and marine waters and at 45–500 μg/L for freshwater depending on water hardness [3]. Zinc is widely used in coating iron and other metals, in wood preservatives, catalysts, photographic paper, accelerators for rubber vulcanisation, ceramics, textiles, fertilizers, pigments and batteries [2], and as a consequence it is often found in the wastewaters arising from these processes. The most significant industrial sources arise from electroplating, mining industry effluents and acid mine drainage. For instance, zinc concentrations of over 620 mg/L have been recorded in drainage from abandoned copper mines in Montana, USA [4].

The main techniques currently used for metal removal include chemical precipitation, electrochemical deposition, evaporation, cementation, membrane process, ion-exchange and activated carbon adsorption [5,6]. However, the application of these methods is often limited due to their inefficiency, high capital investment or operational costs. For example, ion-exchange resins and activated carbons are efficient in the removal of a range of metals and exhibit high uptake capacities, but their utilisation may be prohibitively costly for treating large volumes of wastewater. Consequently, there is a growing requirement for novel, efficient and cost-effective techniques for the remediation of metal-bearing wastewaters before their discharge into the environment.

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Over the last two decades, one approach which has shown considerable potential for metal removal from aqueous media is biosorption, i.e. the use of natural or raw materials and wastes from industrial and agricultural activities to adsorb metals from aqueous solutions [4,7]. A number of metal-binding mechanisms have been postulated in biosorption including chemisorption by ion-exchange, complexation, coordination, chelation, physical adsorption and micro-precipitation [4]. A number of studies have evaluated the application of biosorption for the removal of Zn^{2+}. These include the use of natural materials such as moss [8], peat [9,10], zeolite and bentonite [11], tree leaves [12], mixed mineral [13,14]; microbial and algal biomass [4,15] including seaweed, yeast, fungi, bacteria; industrial and agricultural wastes [7,16–20] such as peanut hulls, corncobs, cornstarch, hazelnut shells, waste tea leaves, blast furnace slag, sea nodule residue, sugar beet pulp, lignite, lignin and powdered waste sludge, etc. Despite the relative simplicity and potential cost-effectiveness of biosorption, metal removal using low-cost biosorbents is relatively unproven and needs further development before it may be applied routinely in practice and thus considered an alternative to use of ion-exchange resins or activated carbons.

Crab carapace is an abundant natural waste product from seafood processing with millions of tons being generated annually [21]. The chemical compositions of crab carapace were known to be in the ranges of 40–66% calcium carbonate, 3–5% magnesium carbonate, 11–29% protein, 20–27% chitin, 1.35% lipid and less than 2% others as dry weight basis [22,23]. It is widely used in the manufacture of cosmetics and personal care products. Recently, it has been recognised that crab carapace has significant potential as a biosorbent for metal removal after simple pre-treatment [4,24–33]. For example, the uptake of Pb^{2+} by crab carapace (*Protunus tritubercularus*) has been reported to be 1300 mg/g [34,35]. An *et al.* [36] evaluated the capacity of crab carapace (*Chinonecetes opilio*) to treat several heavy metal ion solutions (Pb^{2+}, Cd^{2+}, Cu^{2+} and Cr^{2+}) and demonstrated that crab carapace was more efficient than cation exchange resin, zeolite and powdered or granular activated carbon.

In this work, we investigated the potential of crab carapace from the edible crab *Cancer pagurus* to act as a biosorbent for Zn^{2+} removal from aqueous media. Crab carapace was prepared in the particle size ranges of 0.25–0.8 mm and 0.8–1.5 mm and used in batch studies to quantify the effects of agitation speed, contact time, pH and metal concentration on Zn^{2+} uptake performance. Binary-metal studies were carried out to investigate the effect of Cu^{2+} or Pb^{2+} on Zn^{2+} uptake. Sequential-batch process and fixed-bed column studies were conducted to compare performance under dynamic conditions. Finally, the uptake of Zn^{2+} by crab carapace was compared with those of other biosorbents, activated carbons and commercial ion-exchange resins.

2. Materials and methods

2.1. Biosorbent preparation

Commercially milled crab carapace from the edible crab (*Cancer pagurus*) was supplied by Carafiltration Ltd. (York, UK). This carapace had been ultrasonically cleaned and cryogenically milled (−120 °C). The material was mechanically sieved to give particles in the ranges of 0.25–0.80 mm ('small') and 0.80–1.50 mm ('large'). These fractions were washed with deionised water to remove residual scale and dust and then oven-dried at 40–60 °C. The specific surface area of small and large particles was determined by the Brauner Emmett and Teller (BET) single point method using nitrogen gas to be 33.4 and 30.5 m^2/g, respectively.

2.2. Batch experiments

Metal ion solutions were prepared from zinc sulphate ($ZnSO_4{\cdot}7H_2O$, BDH-AnalaR), lead nitrate ($Pb(NO_3)_2$, BDH-AnalaR), and copper sulphate ($CuSO_4$, anhydrous 98%, Acros Organics). In the case of binary-metal studies, zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$, BDH-GPR) was used instead of zinc sulphate. Batch experiments were conducted in a series of 150 mL HDPE bottles at room temperature (20 ± 2 °C). The pH of solution was measured using a Jenway ion-meter (Model 3340).

In order to investigate the effect of agitation speed and contact time, experiments were performed by mixing 0.25 g crab carapace with 100 mL of a 100 mg Zn^{2+}/L solution (initial pH 4.3) in a series of bottles which were mechanically agitated at a range of speeds (100, 200, 350 and 450 rpm) using a benchtop orbital shaker (IKA®KS 260 basic). Samples were collected at defined time intervals up to 24 h and filtered through 0.45 μm cellulose acetate membrane filters. All samples were preserved by addition of 50 μL of 1 + 1 HCl (dilution of concentrated HCl solution with the same volume of deionised water) per 10 mL sample and stored at 4 °C until analysed. Concentrations of Zn^{2+} and Mg^{2+} were determined by flame atomic absorption spectrometry (Model 357), and Ca^{2+} by flame spectrophotometer (Sherwood, Model 410). Control experiments were conducted under the same experimental conditions using deionised water instead of Zn^{2+} solutions. In each case the quantity of metal adsorbed was deduced from a mass balance calculation.

A similar experimental procedure was used to investigate the effect of initial pH of Zn^{2+} solution (at an agitation speed of 350 rpm and contact time of 24 h). The pH of the solution was adjusted in the range 2–7 using 0.1 M HCl or 0.1 M NaOH. In order to investigate the effect of initial Zn^{2+} concentration, the same experimental conditions (initial pH 4.3) were applied and the initial Zn^{2+} concentration varied in the range 10–460 mg/L. In investigating the effect of the presence of other metal ions on Zn^{2+} biosorption, Cu^{2+} and Pb^{2+} solutions were prepared and mixed with Zn^{2+} solutions (initial pH 4.3 of mixed solution) using 0.25 g crab carapace at 350 rpm agitation speed for 24 h. Concentrations of Cu^{2+} and Pb^{2+} were determined by flame atomic absorption spectrometry (Model 357).

2.3. Sequential-batch experiments

These were used to investigate metal uptake capacity of crab carapace in single (Zn^{2+}, Cu^{2+} and Pb^{2+}) and binary-metal (Zn^{2+}-Cu^{2+}, Zn^{2+}-Pb^{2+}) solutions. The experiments were conducted by mixing 0.25 g of crab carapace with 100 mL of single or binary-metal solutions with initial concentration of 100 mg/L

for each metal and initial pH of 4.3 under 350 rpm agitation speed. After 24 h the liquid was decanted and replenished with a new solution of the metal/metals at the same initial concentration. This process was repeated five times. Upon completion the final pH of the solution was measured and the crab carapace dried and weighed.

2.4. Fixed-bed column experiments

Column experiments were conducted using glass columns (20 or 40 cm depth; internal diameter 2.0 cm). Three sets of experiments were conducted: 88.5 g of 'large' crab carapace particles in a 40 cm depth column (L-40), 42 g 'large' particles in a 20 cm depth column (L-20) and 42 g 'small' particles in a 20 cm depth column (S-20). The Zn^{2+} solution (100 mg Zn^{2+}/L) was pumped (Watson-Marlow Ltd., model 101U/R) upwards through the column at a flow rate of 10.1–10.3 mL/min. At the top of the column 3 mm glass beads were added to prevent flotation of the crab carapace particles. Effluent samples were automatically collected in 50 mL tubes every 2 or 4 h using a fraction collector (ISCO, Foxy Jr.).

3. Results and discussion

3.1. Effect of agitation speed and contact time

Fig. 1 shows the efficiency of Zn^{2+} removal by crab carapace particles in the ranges of 0.25–0.8 mm (small) and 0.8–1.5 mm (large) over time at four different agitation speeds (100, 200, 350 and 450 rpm). Crab carapace particles in the bottles were virtually stationary at 100 rpm agitation, gently agitated at 200 rpm, and thoroughly mixed with solution at 350 and 450 rpm. It is evident that the removal efficiency of Zn^{2+} increased significantly at agitation speeds between 100 and 350 rpm. Use of agitation speeds in excess of 350 rpm resulted in no significant increase in removal efficiency.

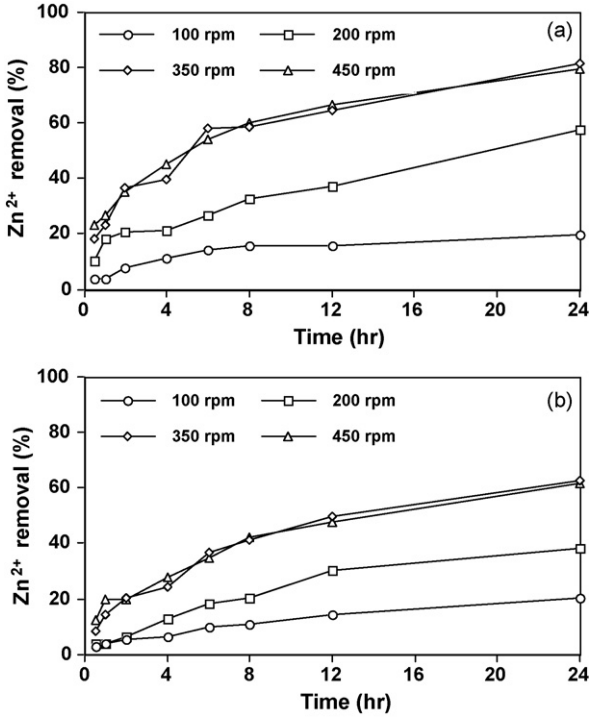

Fig. 1. Zn^{2+} removal efficiencies by crab carapace over 24 h at agitation speeds of 100, 200, 350 and 450 rpm: (a) small particle size; (b) large particle size.

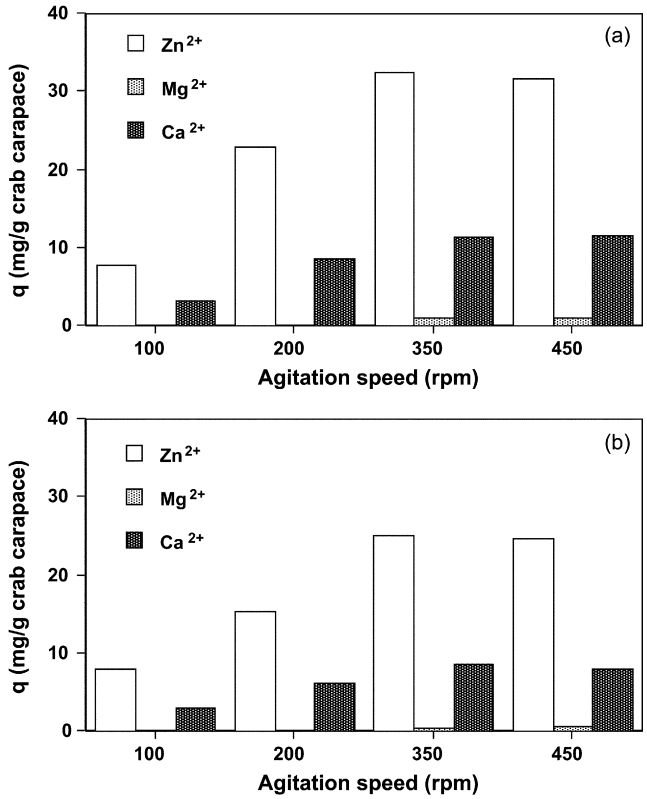

Fig. 2. Zn^{2+} uptake and Ca^{2+} and Mg^{2+} elution at agitation speeds of 100, 200, 350 and 450 rpm after 24 h contact time: (a) small particle size; (b) large particle size.

At an agitation speed of 350 rpm and after a contact time of 24 h, Zn^{2+} removal reached 81.3% and 62.8% for small and large crab carapace particles, respectively. The concentrations of Ca^{2+} and Mg^{2+} ions in the resultant solution after 24 h agitation were also determined (Fig. 2). The release of sodium and potassium ions was negligible. As with the uptake of Zn^{2+}, the elution of Ca^{2+} or Mg^{2+} increased with agitation speed over the range of 100–350 rpm, but showed no further increase above 350 rpm for both particle sizes. After 24 h of agitation at 350 rpm, Zn^{2+} uptakes of 32.5 and 25.1 mg/g crab carapace were reached, and 11.3 and 8.6 mg/g of Ca^{2+} and 1.0 and 0.4 mg/g of Mg^{2+} were eluted due to dissolution of calcium and magnesium carbonates and ion-exchanges for small and large crab carapace particles respectively. The Ca^{2+} and Mg^{2+} elution from control study of crab carapace mixed with deionised water were subtracted in calculation.

It is obvious that at lower agitation speed there was insufficient energy for Zn^{2+} to permeate the intraparticular surface for adsorption, forming micro-precipitation, chelation or ion-exchange. Similarly, Evans, et al. [26] also suggested that following the initial adsorption stage the rate of Cd^{2+} uptake

by chitosan-based crab carapace was controlled by intraparticle diffusion in their study. Hence, it can be postulated that effective dispersion of crab carapace maintained the high mass transfer in the batch reactor was one of the key conditions for improving Zn^{2+} removal.

Crab carapace consists of 20–27% chitin, a natural polysaccharide comprising of (1–4)-2-acetamido-2-deoxy-D-glucose units. It is believed that adsorption of Zn^{2+} in this study took place on the surface sites within the chitin microporous matrix [21]. At the same time, the presence of calcium carbonate, a major component of crab carapace, and magnesium carbonate also dissolved in the mixture and released Ca^{2+}, Mg^{2+} and CO_3^{2-}. However, as Lee et al. [23] suggested that total released Ca^{2+} was not contributed only through $CaCO_3$ dissolution, the ion-exchange between Ca^{2+} and tested metal ions also promoted Ca^{2+} release in their study with Pb^{2+} removal by crab carapace. On the other hand, the released CO_3^{2-} reacted with proton to form HCO_3^- and H_2CO_3, hence improved solution pH [23,28,34,35]. Therefore Zn^{2+} removal was resulted in the formation of metal-carbonate precipitates such as $ZnCO_3{\cdot}2Zn(OH)_2{\cdot}H_2O$ [37]. In addition, with the dissolution of $CaCO_3$ and $MgCO_3$, the functional groups of chitin such as $NHCOCH_3$ band and others such as CO_2 band on the crab carapace surface were exposed, and these functional groups are effective in the adsorption of precipitates on the surface of crab carapace [29,32,34]. Therefore, it can be demonstrated that biosorption of Zn^{2+} by crab carapace proceeds via a complex range of processes including adsorption, micro-precipitation and ion-exchange.

3.2. Effect of initial pH

The effect of initial pH on Zn^{2+} uptake and elution of Ca^{2+} and Mg^{2+} ions was examined over the range pH 2–7 (Fig. 3). The zinc species fraction under different pH condition is also shown in Fig. 4. Under pH lower than 7.5, zinc is dominantly exists in divalent ion form and there is no $Zn(OH)_2$ precipitation happen. Within the initial pH range of 2–4, the final pH of the solution increased 3–4 units over the initial conditions and Zn^{2+} uptake by crab carapace increased, i.e. removal highly dependent on pH. In contrast, over the pH range 4–7, the final pH was relatively constant at 7 and there was no significant difference of Zn^{2+} uptake observed, i.e. removal independent of pH.

At an initial pH of 2.0, where Zn^{2+} uptake was negligible, Ca^{2+} and Mg^{2+} elution were significant, reaching 235.4 mg Ca^{2+}/g and 19.3 mg Mg^{2+}/g for both small and large particles. Lee et al. [23] have studied calcium carbonate in crab shell for different final solution pH. Their results showed that under lower final pH condition, $CaCO_3$ dissolved as Ca^{2+} and CO_3^{2-}, and CO_3^{2-} further reacted with proton to form HCO_3^- and H_2CO_3. Therefore, at lower initial pH condition, Zn^{2+} could not combine with CO_3^{2-} to form $ZnCO_3$. Even though the dissolution of $CaCO_3$ and $MgCO_3$ could expose more functional groups of chitin available for metal ions adsorption, Kim and Park [28] concluded that chitin or chitosan could only adsorb limited Pb^{2+} which was much lower than the removal by precipitation at the initial solution pH of 5. On the other hand, under acidic conditions, ion-exchange between Zn^{2+} and Ca^{2+} or Mg^{2+} suppressed and the concentration of protons exceeds that of Zn^{2+} and hence out-competes Zn^{2+} ions to occupy the binding sites on the crab carapace, leaving Zn^{2+} ions free in solution. Hence, the optimal initial pH of Zn^{2+} solution for biosorption by crab carapace should be above 4.

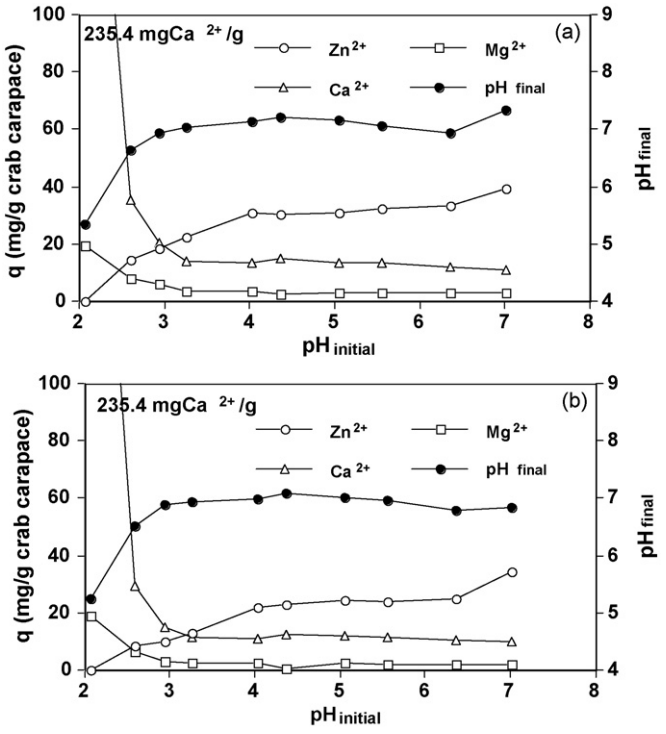

Fig. 3. Zn^{2+} uptake and Ca^{2+} and Mg^{2+} elution under different initial pH conditions: (a) small particle size; (b) large particle size.

3.3. Effect of initial Zn^{2+} concentration

The results shown in Fig. 5 demonstrate that Zn^{2+} uptake increased with metal concentration but that the removal efficiency decreased. At an initial concentration of 460 mg Zn^{2+}/L, Zn^{2+} uptake reached 90.8 and 60.0 mg/g for small and large particles, respectively, i.e. three times those measured at the initial concentration of 100 mg Zn^{2+}/L.

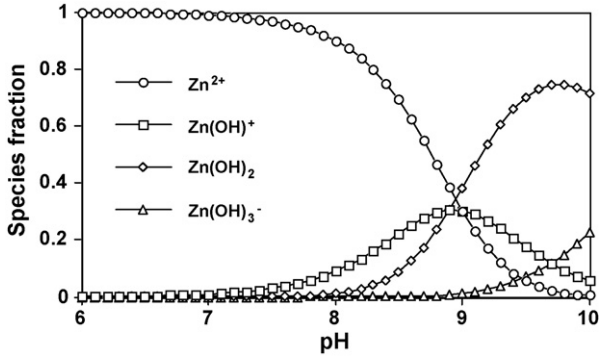

Fig. 4. Zinc species fraction under different pH condition.

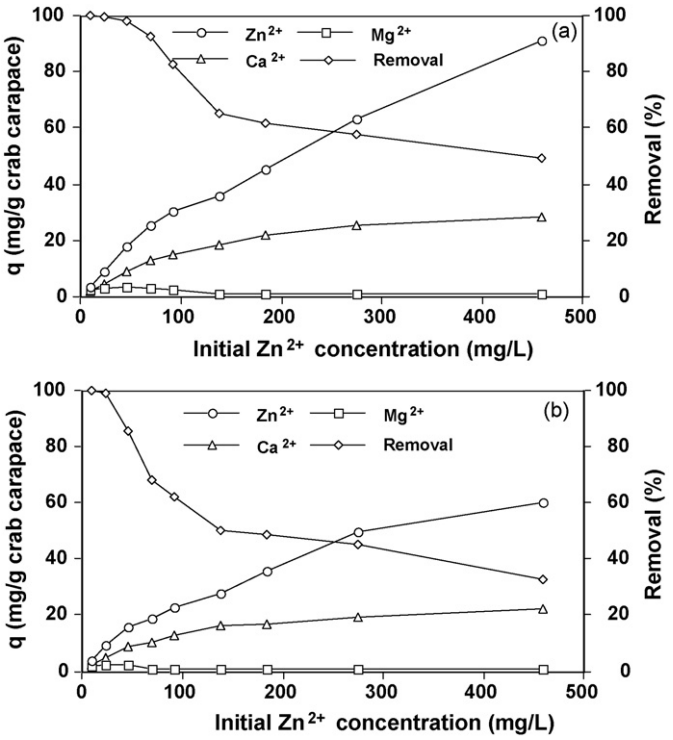

Fig. 5. Zn^{2+} uptake and Ca^{2+}, Mg^{2+} elution under different initial Zn^{2+} concentrations: (a) small particle size; (b) large particle size.

When the initial Zn^{2+} concentration was increased from 10 to 140 mg/L, the removal efficiency decreased rapidly from both over 99% to 65.2% and 50.1% for small and large crab carapace particles, respectively, then further decreased to 49.5% and 32.7% when the initial Zn^{2+} concentration increased to 460 mg/L. Increasing the initial Zn^{2+} concentration increased the release of Ca^{2+} which then remained approximately constant at concentrations greater than 140 mg/L. Less Mg^{2+} was released than Ca^{2+} in both crab carapace particles experiments (Fig. 5). Therefore, it can be concluded that under lower Zn^{2+} concentrations (< 140 mg/L) ion-exchange mechanism contributed part to the zinc removal along with micro-precipitation by forming $ZnCO_3$ through the dissolution of $CaCO_3$. In contrast, under higher concentrations (>140 mg/L) Zn^{2+} uptake caused by ion-exchange and formation of $ZnCO_3$ was limited and other mechanisms such as adsorption, cheletion and micro-precipitation by forming $Zn(OH)_2$, etc. might be predominant for the enhancement of Zn^{2+} removal. Further investigations on micro-precipitation mechanism are recommended in future studies.

3.4. Effect of binary-metal solution

The influence of the presence of other metal ions (Cu^{2+} and Pb^{2+}) on Zn^{2+} removal by crab carapace (0.25 – 0.8 mm particles) was investigated. Results indicated that the presence of Cu^{2+} or Pb^{2+} significantly suppressed Zn^{2+} removal (Table 1). Zn^{2+} removal efficiency in the absence of Cu^{2+} or Pb^{2+} was 83.4% but decreased to 39.9%, 35.8% and 22.8% with the increase of initial Cu^{2+} concentration from 25–50 and 100 mg/L, and decreased to 72.8%, 70.1% and 59.7% with the increase of initial Pb^{2+} concentration from 25–50 and 100 mg/L. Meanwhile Cu^{2+} removal efficiency decreased slightly from 99.6% to 96.6% with the presence of 100 mg Zn^{2+}/L. No effect on the removal of Pb^{2+} was observed with increasing Zn^{2+} concentration. These results indicated that preferential affinity of metal ion by crab carapace followed the order: $Pb^{2+} > Cu^{2+} > Zn^{2+}$. This conclusion was also confirmed by results from the sequential-batch experiments reported below.

Table 1
Influence of Cu^{2+} or Pb^{2+} presence on Zn^{2+} removal by small particle crab carapace

Test no.	Initial concentration (mg/L)			Removal efficiency (%)		
	Zn^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}	Cu^{2+}	Pb^{2+}
1	0	100		–	99.57	
2	25	100		60.07	98.37	
3	50	100		37.84	97.41	
4	100	100		22.79	96.61	
5	100	50		35.76	97.18	
6	100	25		39.92	95.18	
7	100	0		83.41	–	
8	50	50		59.12	98.66	
9	25	75		64.15	98.45	
10	0		100	–		98.14
11	25		100	96.64		99.78
12	50		100	85.69		100.00
13	100		100	59.70		99.44
14	100		50	70.13		100.00
15	100		25	72.79		100.00
16	100		0	83.41		–
17	50		50	90.72		100.00
18	25		75	97.33		100.00

3.5. Sequential-batch experiments

The sequential-batch process may be considered an effective and efficient option for evaluating the practical application of the biosorption technique. In this study, single (Zn^{2+}, Cu^{2+}, Pb^{2+}) and binary-metal (Zn^{2+}–Cu^{2+}, Zn^{2+}–Pb^{2+}) solutions were treated with both small and large crab carapace particles. Fig. 6 shows the accumulated uptakes of Zn^{2+}, Cu^{2+} and Pb^{2+} on small and large crab carapace particles after each batch test and Tables 2a and 2b show the removal efficiencies in each step.

Zn^{2+} removal efficiencies decreased with each step of the sequential process (from 83.2% in the first to 31.2% in the fifth). The sequential reduction in removal efficiency was lower for Cu^{2+} (from 99.4% to 71.9%) and there was no significant decrease for Pb^{2+}. In binary-metal studies, Zn^{2+} biosorption was greatly suppressed by the presence of Pb^{2+} or Cu^{2+}, and the results from Zn^{2+}–Cu^{2+} binary solution showed negative Zn^{2+} removal in the last three batches, i.e. occurrence of Zn^{2+}desorption in studies using small particles. Meanwhile, Cu^{2+} removal showed a slight decrease in the binary-metal sorption compared with single Cu^{2+} solution, whereas, Pb^{2+} was removed nearly completely under all conditions even after five batch tests. These results were strongly comparable to the results in Table 1.

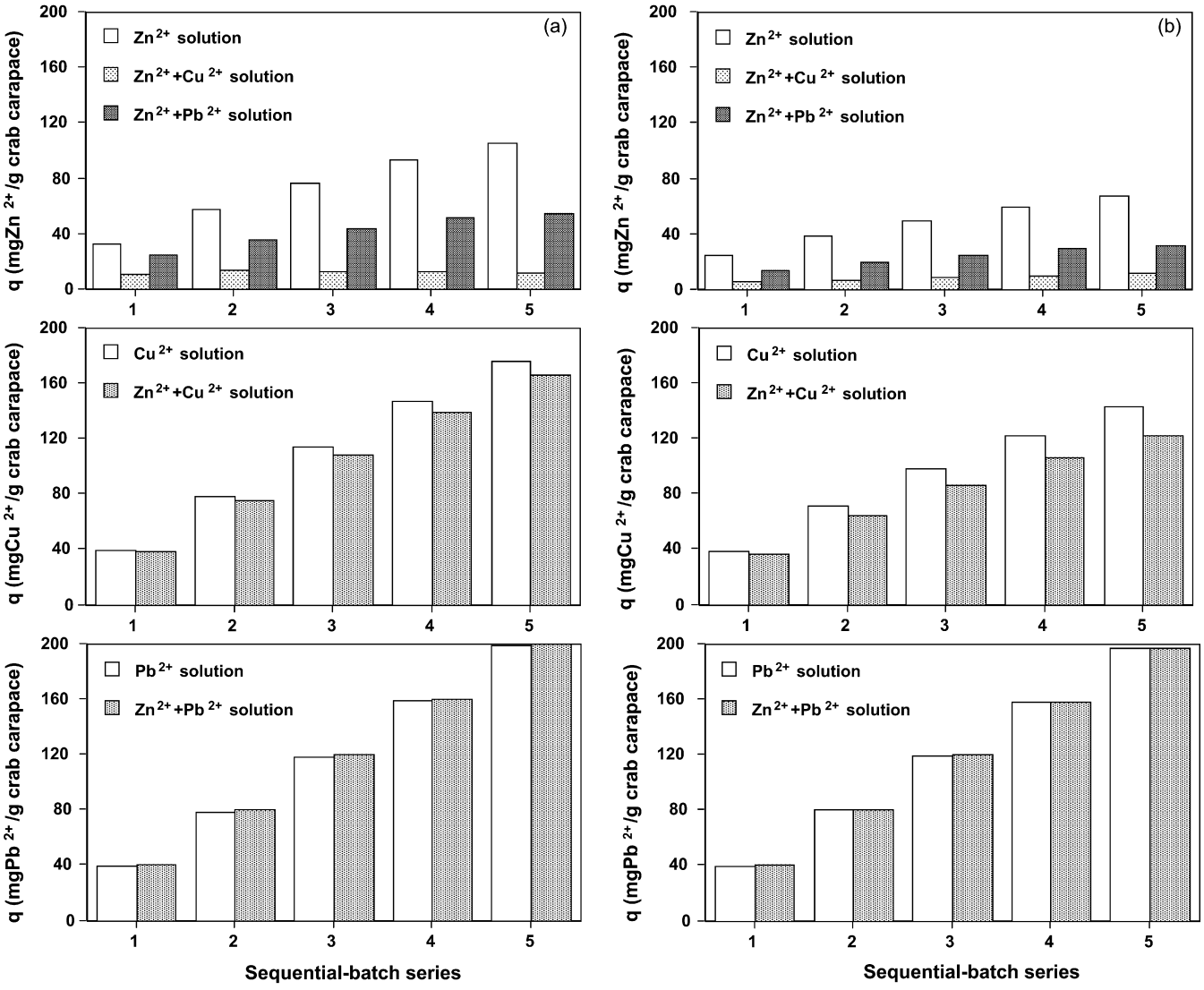

Fig. 6. Zn^{2+}, Cu^{2+} and Pb^{2+} accumulated uptakes by crab carapace in sequential-batch experiments: (a) small particle size; (b) large particle size.

The suppression of Zn^{2+} biosorption in the binary-metal solution is also evident from Fig. 6. For Zn^{2+} alone, the accumulated uptake reached 105.6 and 67.6 mg/g after five sequential-batches for small and large crab carapace particles, respectively. The presence of Pb^{2+} reduced Zn^{2+} uptake to 55.0 and 32.3 mg/g while the presence of Cu^{2+} reduced Zn^{2+} uptake significantly to 11.6 and 11.7 mg/g for small and large particles, respectively.

Table 2a
Zn^{2+}, Cu^{2+} and Pb^{2+} removal efficiencies in sequential-batch process by small crab carapace particles

	Removal (%)					Final pH	Weight change (%)
	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5		
Single metal solution							
Zn^{2+}	83.15	60.83	46.65	42.10	31.15	6.3	−5.05
Cu^{2+}	99.36	96.73	89.63	80.42	71.91	5.6	−4.91
Pb^{2+}	97.44	99.03	99.44	99.63	99.97	7.9	+6.39
Zn^{2+}–Cu^{2+} binary metal solution						5.7	−5.69
Zn^{2+}	26.68	9.23	−3.55	−0.70	−2.70		
Cu^{2+}	96.64	91.82	81.98	75.61	67.84		
Zn^{2+}–Pb^{2+} binary metal solution						6.3	+3.43
Zn^{2+}	61.64	28.32	19.08	19.43	9.02		
Pb^{2+}	100	99.65	99.62	99.68	99.49		

Table 2b
Zn^{2+}, Cu^{2+} and Pb^{2+} removal efficiencies in sequential-batch process by large crab carapace particles

	Removal (%)					Final pH	Weight change (%)
	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5		
Single metal solution							
Zn^{2+}	62.02	34.26	28.64	25.01	18.99	6.1	−8.67
Cu^{2+}	95.96	81.67	67.20	60.62	52.09	5.4	−6.85
Pb^{2+}	99.29	99.84	99.31	95.59	96.68	6.8	−0.55
Zn^{2+}–Cu^{2+} double metal solution						5.4	−7.71
Zn^{2+}	15.15	3.38	4.11	3.38	3.34		
Cu^{2+}	91.17	68.47	55.90	49.53	39.32		
Zn^{2+}–Pb^{2+} double metal solution						5.9	−0.67
Zn^{2+}	34.36	15.31	13.17	10.82	7.15		
Pb^{2+}	99.97	99.76	99.35	95.39	97.44		

With the single metal solutions the uptake of Pb^{2+} and Cu^{2+} after five sequential-batches reached 198.2 mg Pb^{2+}/g, 175.2 mg Cu^{2+}/g and 196.3 mg Pb^{2+}/g, 143.0 mg Cu^{2+}/g for small and large particles, respectively (Fig. 6). It may also be noted from Fig. 6 that the crab carapace still had capacity for more Cu^{2+} or Pb^{2+} removal. Cu^{2+} uptake was slightly decreased in the presence of Zn^{2+}, but for Pb^{2+} there were no differences in uptake either with or without the presence of Zn^{2+}. These results are consistent with the results shown in Table 2 and confirmed that the preferential affinity of metal ions by crab carapace followed the order of $Pb^{2+} > Cu^{2+} > Zn^{2+}$.

It is noteworthy that the final pH of all solutions after the sequential-batch studies increased 1–2 units from the initial pH of 4.3, except for the Pb^{2+} solution in which the final pH was 7.9 and 6.8 for small and large particle studies, respectively. In addition, after the sequential-batch studies the mass of crab carapace had been reduced by approximately 5% and 8% for small and large crab carapace particles. This was observed under all experiments except those with Pb^{2+}, which showed an increase in weight in the experiments with small particles and nearly no change when large particles were used. It is believed that the elution of Ca^{2+} and Mg^{2+} from crab carapace resulted in the loss weight. However, we also found that fine white powder appeared in solution with the crab carapace in the experiments with Pb^{2+}. As postulated by Kim and Park [28] and Lee et al. [34], we believe that this was due to precipitation of $Pb_3(CO_3)_2(OH)_2$. Precipitation is the main mechanism for Pb^{2+} removal rather than ion-exchange with Ca^{2+} and Mg^{2+}, therefore no weight reduction was observed. Another reason was owe to the much higher atomic mass of lead compared that of Ca or Mg.

3.6. Fixed-bed column process

Compared to the sequential-batch process, column systems provide continuous operation and the potential for straightforward automated control in their application. In this study, three column experiments were conducted to investigate the removal of Zn^{2+} by crab carapace. The performance of the three columns is shown in Fig. 7 and the results summarised in Table 3. In Fig. 7, plots of C_i/C_o (C_i, Zn^{2+} concentration in effluent; C_o, Zn^{2+} concentration in influent) versus the number of bed volumes indicate significant differences from the "typical" breakthrough curve. Unlike conventional sorbents such as activated carbon or ion-exchange resin, the breakthrough occurred soon after the start of the process. The curve then increased gradually but complete exhaustion ($C_i/C_o = 1.0$) was never reached. This was consistent with results from our batch studies at various agitation speeds, i.e. the energy for Zn^{2+} permeating the intraparticular surface

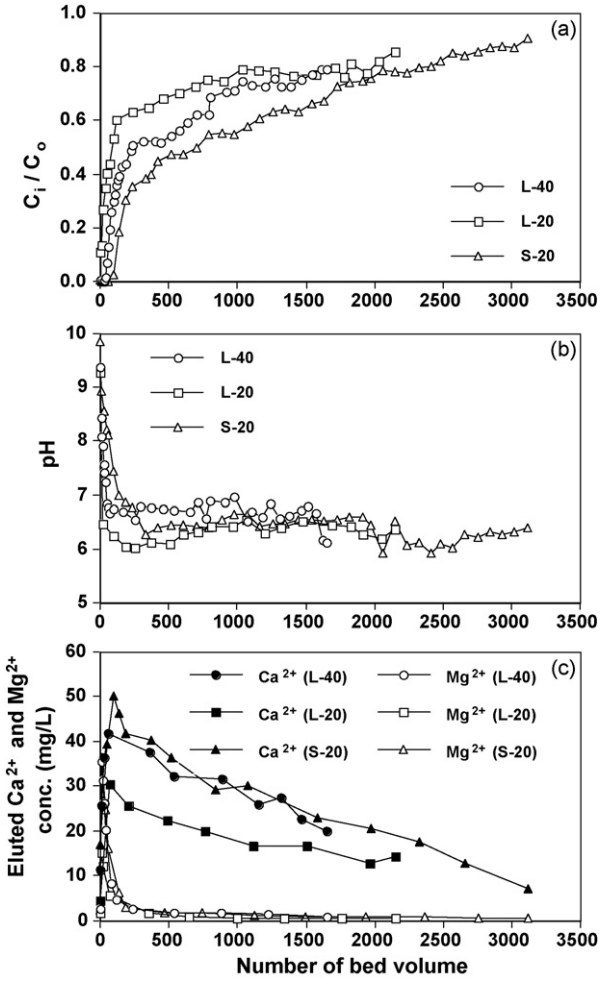

Fig. 7. Column performance: (a) C_i/C_o; (b) effluent pH and (c) eluted Ca^{2+} and Mg^{2+}.

Table 3
Summary of column performances

Column type	Crab carapace weight (g)	Flow rate (mL/min)	Volume of treated solution (L)	Zn removed (g)	Average uptake (mg/g)	Ca elution (g)	Mg elution (g)
L-40	88.5	10.3	175.51	6.89	77.88	5.06	0.47
L-20	42	10.2	113.83	3.07	72.97	2.07	0.13
S-20	42	10.1	165.02	5.94	141.32	4.01	0.28

and the contact time between Zn^{2+} and crab carapace in column process was limited. Using a threshold of $C_i/C_o = 0.8$, L-40, L-20 and S-20 columns treated 1660, 1620 and 2410 bed volumes, respectively. This corresponded to treated volumes of 175.5, 113.8 and 165.0 L of 100 mg Zn^{2+}/L, and equated to Zn^{2+} uptakes of 77.9, 73.0 and 141.3 mg/g, respectively. It may be noted that the uptake by small particles was approximately double that of the large particles, even though the difference between the specific surface area of small and large particles of carapace was only around 10%. This result indicated that Zn^{2+} uptake was not proportional to the specific surface area, further elucidating Zn^{2+} was not simply removed through monolayer adsorption, and other removal mechanisms such as ion-exchange and micro-precipitation must be included.

Shortly after commencement, the pH of the effluent reached 9 and then rapidly decreased to 6–7, which was still about 2–3 pH units higher than the influent (pH 4.3). In addition, Ca^{2+} and Mg^{2+} elution was most significant at the beginning but gradually decreased with time, as shown in Fig. 7. Their elution resulted from ion-exchange with protons and Zn^{2+}. By the end of the study, 5.06, 2.07 and 4.01 g Ca^{2+}, and 0.47, 0.13 and 0.28 g Mg^{2+} were eluted from the L-40, L-20 and S-20 columns, respectively, causing 5–6% weight loss in large crab carapace particles and ~10% loss of small particles.

The gradient in Zn^{2+} uptake along the column height was also investigated in the S-20 column. Crab carapace was segmented from the bottom, 5, 10 and 15 cm up of the bottom, and the top sections, washed with deionised water twice and completely dried in the oven at 60 °C. This crab carapace (0.25 g in triplicate) was mixed with 0.1 M HCl (100 mL) and shaken for 2 h and the supernatant analysed for Zn^{2+}. The mean results were used for Zn^{2+} uptake calculations (Fig. 8). It is clear that complete saturation of the crab carapace occurred in the lowest 5 cm of the column bottom (172.5 mg/g), while uptake gradually decreased

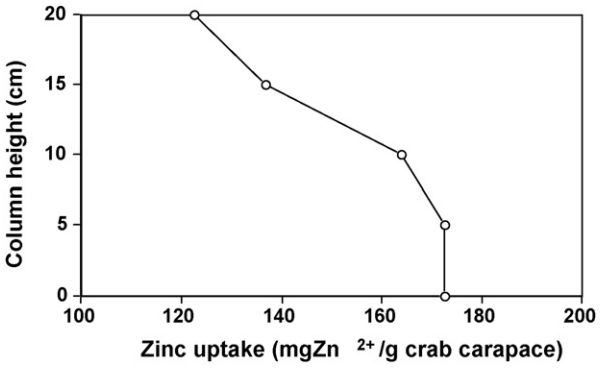

Fig. 8. Zn^{2+} uptake profile along the S-20 column depth.

Table 4
Comparison of Zn^{2+} uptake capacity of selected materials

Bio-sorbent	Zn^{2+} uptake (mg/g)	Reference
Natural material		
Bentonite	52.91	[11]
Red mud	12.59	[9]
Peat	9.28–12.1	[16]
Microbial and algal biomass		
Bacillus subtilis	137	[4]
Fungal biomass	98	[4]
Sargassa sp.	70	[4]
Manganese oxidising bacteria	39	[4]
Saccharomyces cerevisiae	14.0–40.0	[4]
Candida tropicalis	30	[4]
Rhizopus arrhizus	14.0–20.0	[4]
Penicillium Chrysogenum	6.5	[4]
Bacillus sp.	3.4	[4]
Penicillium Spinulosum	0.2	[4]
Industrial and agricultural wastes		
Sun flower stalks	30.73	[9]
Lignin	95	[7]
Lignite	22.83	[9]
Scarp rubber	100	[9]
Defatted rice brans	5.0–17.0	[9]
Soybean hulls	4.0–20.0	[9]
Cottonseed hulls	1.0–15.88	[9]
Blast furnace slag	17.65–98.08	[9]
Solid residue of olive mill products	5.4	[9]
Peanut hulls	8.96	[19]
Corncobs	1.96	[19]
Cornstarch	6.86	[19]
Sugar beet pulp	17.78	[19]
Chitosan	58.83	[19]
Sea nodule residue	21.09	[16]
Biosolids	36.87	[17]
Activated carbon		
C	4.01–18.53	[24]
F-400	3.15–11.85	[24]
F-300	6.03	[24]
Centaur HSL	10.08	[24]
Activated carbons	4.61–33.56	[9,21,38,39]
Commercial resins		
Duolite GT-73	55.56	[19]
Amberlite IRC-718	156.89	[19]
Amberlite 200	84.98	[19]
Lewatit TP-207	89.56	[19]
Crab carapace		
0.25–0.8 mm Particles	172.5	This work
0.8–1.5 mm Particles	77.9	This work

with progression up the column (reaching 120 mg/g at the top). The data was highly consistent with the average uptake, as shown in Table 3.

It can be concluded that the small particle size of crab carapace performed better than the large size, and the longer the column was, the more effective and efficient of the Zn^{2+} removal. However, it must be pointed out that even though the Zn^{2+} uptake capacity determined in the column process was higher than that in sequential-batch process, when taking into account of the volume of treated solution, the sequential-batch process is a much more effective and efficient alternative than the column process for the practical application of a biosorption technique.

3.7. Comparison of crab carapace with other bio- and commercial sorbents

Zn^{2+} uptake by crab carapace, as quantified in this study from batch and column experiments, was compared with literature values of other biosorbents, including natural materials [9,11,16], microbial and algal biomass [4], industrial and agricultural wastes [9,19], activated carbons [9,38,39] and some commercial cation exchange resins [19] (Table 4). Although the data collated in Table 4 may not represent equivalent or optimised conditions or with various Zn^{2+} removal mechanisms in each case, it still provides a useful comparison for engineers in their decision of suitable biosorbent selection in engineering practice. Several natural materials showed less than 20 mg Zn^{2+}/g uptake, whereas several industrial and agricultural wastes achieved Zn^{2+} uptakes of only below 25 mg/g. In addition, chitosan and commercial resins showed very efficient Zn^{2+} removal, whereas activated carbons were unexpectedly low, in the range of 3.15 – 33.56 mg/g with various types of activated carbons. However, Volesky [4] concluded that *Bacillus subtilis*, fungal biomass and *Sargassa* species are the most effective. The uptake of Zn^{2+} by crab carapace in this study is comparable with these data. Indeed Zn^{2+} uptake by small crab carapace particles in our study was significantly higher than most of the selected biosorbents, even higher than chitosan and commercial cation exchange resins.

4. Conclusion

This study demonstrates that crab carapace to be an effective biosorbent for the removal of Zn^{2+} and other heavy metals from aqueous media. Complimentary batch and column biosorption studies concluded that all parameters such as particle size, agitation speed, contact time, initial metal concentration and initial pH had effect on the removal of Zn^{2+}. Mechanism analysis indicates that biosorption of Zn^{2+} by crab carapace proceeds via a complex range of processes including adsorption, ion-exchange and micro-precipitation formation of $ZnCO_3{\cdot}2Zn(OH)_2{\cdot}H_2O$. Binary-metal studies showed that the presence of Cu^{2+} or Pb^{2+} significantly suppressed Zn^{2+} uptake. In sequential-batch process, Zn^{2+} uptake of 105.6 and 67.6 mg/g were recorded for small and large particles, respectively, while this data reached 141.3 and 76.9 mg/g in our fixed-bed column studies. This study demonstrated that the uptake of Zn^{2+} by crab carapace was significantly higher than most of the selected biosorbents, even higher than chitosan and commercial cation exchange resins, and was comparable with *Bacillus subtilis*, fungal biomass and *Sargassa* species. On the other hand, sequential-batch process showed much more effective and efficient than fixed-bed column process. Since crab carapace is abundant and may be produced in biosorbent form at low cost, it has significant potential as an alternative to activated carbons and ion-exchange resins for the remediation of metal-contaminated waters.

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