



Biosorption of Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ ions from aqueous solutions by pretreated biomass of brown algae

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ABSTRACT

In this paper, marine brown algae *Laminaria japonica* was chemically modified by crosslinking with epichlorohydrin (EC₁ and EC₂), or oxidizing by potassium permanganate (PC), or crosslinking with glutaraldehyde (GA), or only washed by distilled water (DW). They were used for equilibrium sorption uptake studies with Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺. The experimental data have been analyzed using Langmuir, Freundlich and Redlich–Peterson isotherms. The results showed that the biosorption equilibrium was well described by both the Langmuir and Redlich–Peterson isotherms. The order of maximum metal uptakes for Cd²⁺, Cu²⁺ and Zn²⁺ was EC₁ > EC₂ > PC > DW > GA, but the uptakes of Ni²⁺ are almost the same for these sorbents. Moreover, sorption kinetics has been performed and it was observed that the equilibrium was reached in less than 2 h, which could be described by pseudo-first-order kinetic model. The metal adsorption was strictly pH dependent. The optimum pH values of four metals were in the range of 4.3–6.5 for all sorbents, and the optimum solid/liquid ratio was 3.0 g L⁻¹.

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1. Introduction

Many industries discharge heavy metals such as lead, cadmium, copper, nickel and zinc in their wastewaters [1,2]. Therefore, several technologies for treating contaminated wastewater, such as chemical precipitation, oxidation/reduction, ion-exchange, electrolysis and membrane filtration, have been used recently [3]. However these methods are expensive and potentially risky due to the possibility of hazardous by-products generation [4]. Biosorption has provided an alternative treatment of industrial effluents from that of the traditional physico-chemical methods [5,6]. The biological materials that have been investigated for heavy metal uptake include bacteria, fungi, yeast and algae [7–14]. Macroalgae, especially brown algae, have been found to be very effective biosorbents in removing heavy metals from wastewater because of their high uptake capacities, similar to commercial ion-exchange resins and their availability in nearly unlimited amounts from the ocean. *Laminaria japonica*, an abundant waste product in China can be economically used as a potential biosorbent for heavy metals removal from aqueous solutions. The raw algae were chem-

ically pretreated in order to reinforce it for sorption process applications and also to enhance the sorption performance. Pretreatment may be in terms of hardening the cell wall structure through a crosslinking reaction using glutaraldehyde, or increasing the negative charge on the cell surface by NaOH treatment, or opening of the available sites for the adsorption by acid treatment, and enhancing ion-exchange by Ca²⁺ solution treatment [15–19]. Recently, our group has used epichlorohydrin and potassium permanganate to pretreat the raw brown algae *L. japonica* [20]. The results indicated that the pretreated alga has much potential as a biosorbent for the removal of heavy metals from wastewaters.

In this paper, marine brown algae *L. japonica* was chemically modified by epichlorohydrin, potassium permanganate or glutaraldehyde. Biosorption performance of different types of biomass for removal of Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ ions has been studied. Optimization of the sorption process requires a better understanding of controlling environmental parameters, thus, the influences of adsorption time, initial pH values and solid/liquid (s/l) ratio on metal sorption have been investigated. The biosorption capacities were evaluated using Langmuir, Freundlich and Redlich–Peterson isotherms and the results indicated that the pretreated algae are suitable materials for the development of high capacity biosorbents for heavy metal removal.

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2. Materials and methods

2.1. Biomass and chemical modification

A brown alga, *L. japonica*, was sampled at Qingdao, PR China in May 2004. Biomass was dried in an oven at 40 °C to constant weight, ground and sieved into fraction. The 0.30–0.45 mm particle size fraction was used in our experiments.

- Epichlorohydrin crosslinking (EC): ten grams of powdered biomass was taken into a flask together with 150 mL of dimethyl sulphoxide (DMSO) and stirred for 24 h at room temperature. Then 20 mL of epichlorohydrin was added to the mixture to undergo the crosslinking reaction at 20 °C for 2 h. 25 mL of 5 mol L⁻¹ NaOH solution was added and stirred for 5 h at 50 °C. After cooling down to room temperature, it was filtered and washed with 70% 2-propanol in water (800 mL) followed by 0.5 mol L⁻¹ HCl and finally with 70% 2-propanol in water (500 mL) to neutral pH. The sample was kept to dry in an oven at 60 °C overnight, hereafter abbreviated as EC₁. In order to reduce the cost, another sample was obtained by the above pretreatment only with one change of 20% 2-propanol in water (1000 mL) instead of 70% 2-propanol in water, hereafter abbreviated as EC₂.
- Potassium permanganate (PC) oxidized: a modified procedure of Jeon was used [21]. Powdered biomass (10 g) was oxidized in 300 mL of 10 mM KMnO₄ solution at 30 °C for 30 min. Reacted mixture was separated by centrifugation and washed thoroughly with distilled water and dried in an oven at 60 °C.
- Glutaraldehyde crosslinking (GA): a modified procedure of Griffith was used [22]. 10 g of powdered biomass was reacted with 1 M amount of glutaraldehyde (assuming biomass consists of 100% glucose) in 200 mL diluted hydrochloric acid. The mixture was left at room temperature for 3 days, filtered and the biomass washed first with distilled water, then with 0.5% (w/v) sodium carbonate and finally with distilled water. Finally, it was dried in an oven at 60 °C.
- Raw alga (DW): the powdered biomass was washed with distilled water and dried in an oven at 60 °C. To avoid the effect of salt, 10 g of powdered alga was suspended in 500 mL distilled water, stirred for 10 min. Then the biomass was separated by centrifugation. The process was repeated five times till the effluents became almost transparent. The washed biomass was then dried in an oven at 60 °C until a constant weight was reached.

2.2. Biosorption experiments

All chemicals used in this study were of analytical grade (Beijing Beihua Fine Chemicals Co., Ltd., China) and distilled water was used to prepare all solutions. The pH values of the aqueous solution were measured with a pHs-3C model acidity meter (made in Shanghai Precision & Scientific Instrument Co. Ltd., China). In order to adjust the environmental parameters, 0.1 mol L⁻¹ NaCl was used to control the ionic strength and hexamethylene tetramine solution (20%, w/w) was used for keeping proton balance. The stock metal solution was prepared by dissolving corresponding halide into distilled water and 25 mL of NaCl (0.1 mol L⁻¹) and 25 mL of hexamethylene tetramine buffer solution (20%, w/w), then diluted to 250 mL with distilled water. The pH of each solution was adjusted with 0.1 mol L⁻¹ NaOH and HCl.

Unless otherwise stated, 15 mg of each biosorbent was placed in a 50 mL Erlenmeyer flask and treated with 15 mL of metal ions solution. The flasks were incubated in a rotary shaker, at 25 ± 2 °C. Solution samples were filtered through filter papers. The concen-

trations of metal ions were determined by standard EDTA titration.

The amount of heavy metal ions adsorbed at equilibrium, q (mmol g⁻¹), which presents the metal uptake, was calculated from the difference in metal concentration in the aqueous phase before and after biosorption, according to the following equation:

$$q = \frac{(C_0 - C_f)V}{M} \quad (1)$$

where V is the volume of metal solution (mL), C_0 and C_f are the initial and equilibrium concentration of heavy metal in solution (mmol L⁻¹), respectively, and M is the mass of dry biosorbents (mg). Each experiment was repeated three times, and the results are given as averages.

3. Result and discussion

3.1. Effect of pH on metal uptake

The effect of pH on metal biosorption has been studied by many researches, and the results indicated that the pH values of solution could significantly influence biosorption [23,24]. The influence of initial pH on the adsorption characteristics of four metals using biomass after five types of pretreatment methods is shown in Fig. 1. Slight changes were observed for metal ions uptakes within the initial pH range 0.5–2.5. A trend of increasing metal ion binding with increasing pH could be observed for all sorbents for pH values above 2.5. The optimal removal efficiencies of four metals were observed for the pH range 4.3–6.5 for chemically modified and raw brown algae. It is important to note here that the uptakes for some metals may decrease when pH is higher than the optimum pH. So each biomass has its own optimum pH for metal ion uptake. These different behaviours provide a preliminary indication of different metals to be effectively removed at certain pH value.

The pH dependence of metal uptake can be explained considering the nature of biosorbents. The cell wall of brown algae contains a large number of surface functional groups, in which carboxyl is generally the most abundant acidic functional group in the brown algae [25]. At low pH, cell wall ligands are closely associated with hydronium ions and hence the access of the metal ions to the ligands will be restricted. With increasing pH, carboxyl groups would be exposed leading to attraction between these negative charges and the metals and hence increases in biosorption onto the cell surface [26]. The pH effect may be further explained in relation to the competition between H₃O⁺ and metal ions. At low pH values, the concentration of H₃O⁺ far exceeds that of metal ions and hence, occupying the binding sites on the cell walls, leaving metal ions unbound. When the pH was increased, the competing effect of H₃O⁺ decreased and the positively charged metal ions took up the free binding sites. The metal uptake capacity was hence increased [27].

3.2. Biosorption kinetics

The kinetics of metal ions sorption is an important parameter for designing sorption systems and is required for selecting the optimum operating conditions for full-scale batch metal removal process. For all the biosorbents it is observed that 2 h is enough to reach adsorption equilibrium with four metals (Fig. 2). As contact time increases, metal uptakes increase initially, and then become almost stable, denoting attainment of equilibrium. These changes in metal uptake may be due to the fact that, initially, all adsorbent sites were vacant and the solute concentration was high. After that period, only a very low increase in the metal uptake was observed because there are few surface active sites on the cell wall of alga. The quick equilibrium time is due to the particle size. The effective

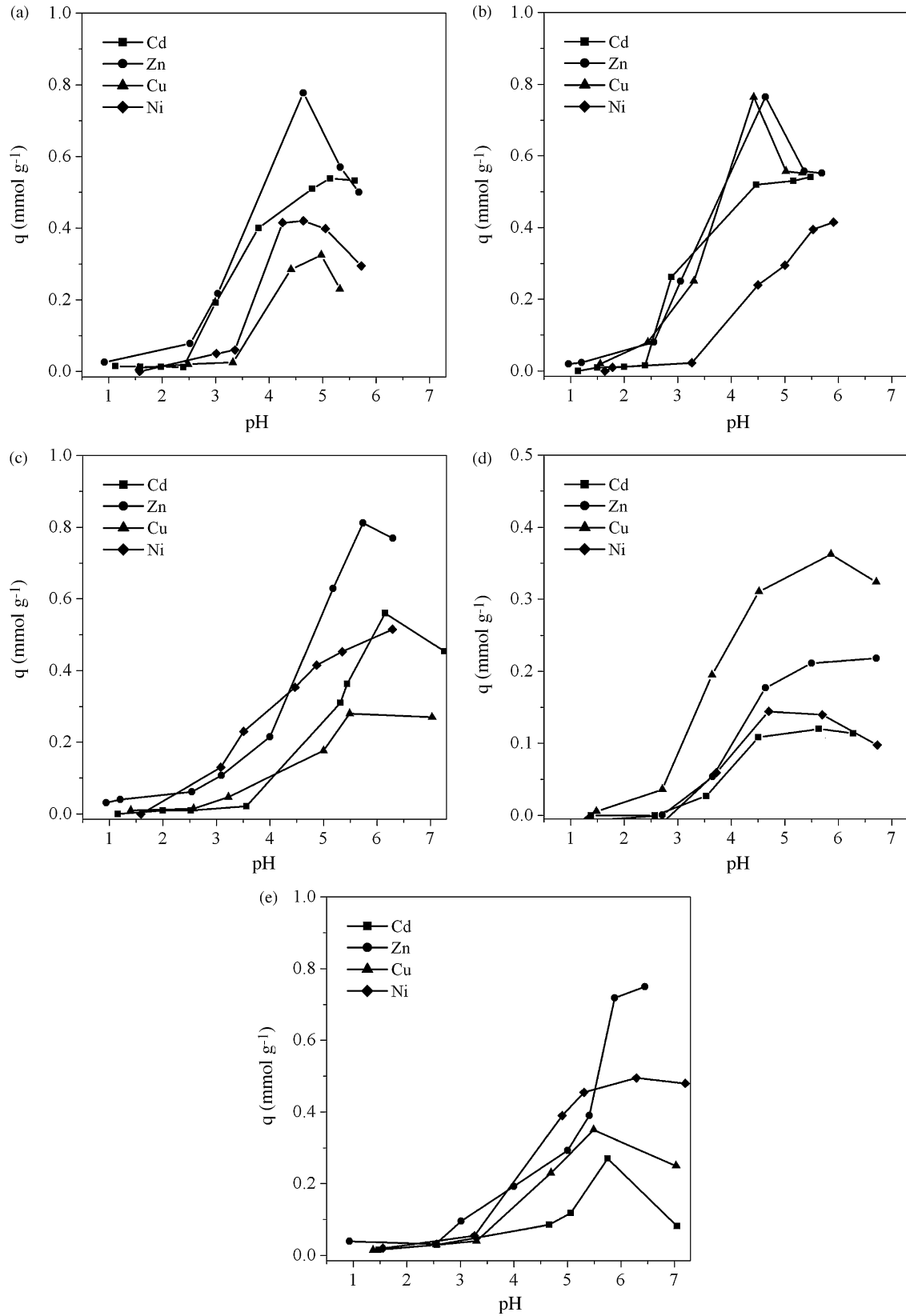


Fig. 1. Effect of pH on biosorption of Cd²⁺, Zn²⁺, Cu²⁺ and Ni²⁺ ions (initial metal concentration 0.90 mmol L⁻¹; s/l ratio 1.0 g L⁻¹; contact time: 180 min) by (a) EC₁, (b) EC₂, (c) PC, (d) GA and (e) DW.

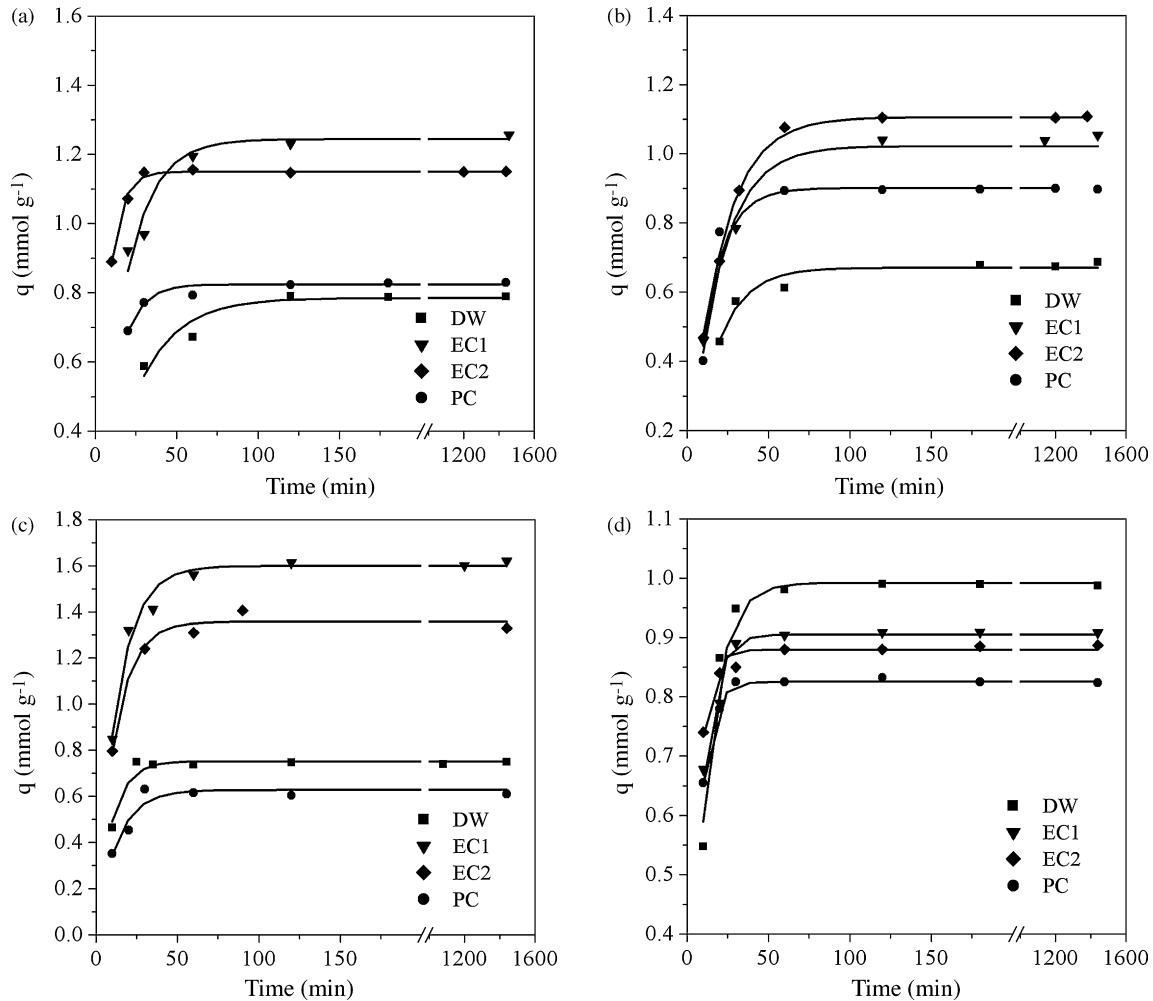


Fig. 2. Kinetics of heavy metals biosorption by chemically modified and raw *Laminaria japonica* biomasses: (a) Cd, (b) Zn, (c) Cu and (d) Ni (initial pH between 4.8 and 6.0; initial metal concentration 4.0 mmol L^{-1} ; s/l ratio 1.0 g L^{-1}).

surface area is high for small particles. The observed rapid kinetics has significant practical importance as it will facilitate the scale-up of the process to smaller reactor volumes ensuring efficiency and economy [28]. To make sure true equilibrium is established, all the subsequent sorption experiments were carried out over 2 h.

Various models can describe the transient behaviour of a batch biosorption process. Most of these have been reported as pseudo-first-order and some as pseudo-second-order kinetic processes [29]. This pseudo-first-order kinetic model known as the Lagergren equation:

$$\ln \left(1 - \frac{q_t}{q_1} \right) = -k_1 t \quad (2)$$

where q_1 and q_t denote the amounts of biosorption at equilibrium and at time t (mmol g^{-1}), and k_1 is the rate constant of first-order sorption (min^{-1}). The pseudo-second-order kinetic model [30]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \quad (3)$$

where q_2 is the amount of biosorption at equilibrium (mmol g^{-1}) and k_2 is the pseudo-second-order rate constant of sorption ($\text{g mmol}^{-1} \text{ min}^{-1}$). The pseudo-first-order and pseudo-second-order kinetics constants for the biosorption of Cd^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} on chemically modified and raw *L. japonica* are tabulated

in Table 1. The correlation coefficients obtained for the pseudo-first-order kinetic model are greater than 0.90 for all metals. The theoretical q_1 values of the pseudo-first-order kinetic model for biomass are close to the experimental values than those of the pseudo-second-order kinetic model. The pseudo-first-order kinetic model fits the experimental data better than the pseudo-second-order kinetic model in this study.

3.3. Adsorption isotherms

The adsorption isotherm models were used to characterize the interaction of metal ions with the algal biomass. Langmuir is the frequently used single-component adsorption model [31], shown below

$$q = \frac{b q_m C_f}{1 + b C_f} \quad (4)$$

where q_m is the maximum metal uptake under the given conditions (complete saturation isotherm-curve plateau) (mmol g^{-1}). In most cases, q_m is the highest possible biomass uptake. b is a constant related to the adsorption energy (L mmol^{-1}). A high value of Langmuir parameter b indicates a steep desirable beginning of the isotherm which reflects the high affinity of the biosorbent for the sorbate [32]. In general, for good biosorbents, high q_m and a steep initial isotherm slope (i.e., high

Table 1

The pseudo-first-order and pseudo-second-order kinetics constants for the biosorption of heavy metals on chemically modified and raw *Laminaria japonica* biomasses (initial pH between 4.8 and 6.0; initial metal concentration 4.0 mmol L⁻¹; s/l ratio 1.0 g L⁻¹)

Sorbent type	Experimental	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
	q_{exp} (mmol g ⁻¹)	R^2	q_1 (mmol g ⁻¹)	k_1 (min ⁻¹)	R^2	q_2 (mmol g ⁻¹)	k_2 (g mmol ⁻¹ min ⁻¹)
Ni							
EC ₁	0.91	0.95	0.91	0.13	0.91	0.93	0.34
EC ₂	0.89	0.94	0.88	0.18	0.95	0.89	0.67
PC	0.83	0.99	0.82	0.16	0.83	0.84	0.55
DW	0.99	0.98	0.99	0.09	0.84	1.02	0.17
Cd							
EC ₁	1.26	0.94	1.24	0.06	0.94	1.28	0.10
EC ₂	1.15	0.99	1.15	0.15	0.84	1.17	0.35
PC	0.83	0.95	0.82	0.09	0.94	0.84	0.32
DW	0.79	0.92	0.79	0.04	0.92	0.82	0.11
Cu							
EC ₁	1.62	0.98	1.60	0.08	0.93	1.66	0.09
EC ₂	1.33	0.96	1.36	0.09	0.88	1.40	0.12
PC	0.65	0.90	0.63	0.08	0.82	0.65	0.23
DW	0.75	0.95	0.75	0.11	0.74	0.77	0.30
Zn							
EC ₁	1.05	0.98	1.02	0.05	0.97	1.06	0.08
EC ₂	1.11	0.99	1.10	0.06	0.94	1.14	0.09
PC	0.90	0.95	0.90	0.08	0.85	0.93	0.14
DW	0.68	0.95	0.67	0.06	0.93	0.69	0.18

b) are desirable [25]. These parameters are evaluated according to the least square fitting method, using the experimental C_f and q values.

The equilibrium experiments were carried out for metal ions Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ by biomass after five types of pretreatment methods (EC₁, EC₂, PC, GA, and DW). The isotherm simulations from the Langmuir model for EC₂ are shown as an example in Fig. 3. Langmuir provided a satisfactory fit with R^2 values ranged from 0.919 to 0.990. The Langmuir model served to estimate the maximum metal uptake values (q_m) where they could not be reached in the experiments. The maximum amounts of metal adsorbed were 1.85, 1.78, 1.13 and 1.42 mmol g⁻¹, respectively for Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺. The results are generally in good agreement with the experimental data. The maximum uptakes of Cd²⁺, Cu²⁺ and Zn²⁺ increased, respectively by 98.9, 83.5 and 71.1% as compared with that of the raw biomass (DW). With regard to Ni²⁺, the sorption

Table 2

A comparison of biosorption capacities of four metals by chemically modified and raw brown algae (initial pH between 4.8 and 6.0; s/l ratio 1.0 g L⁻¹; contact time: 180 min)

Sorbent type	q (mmol g ⁻¹)			
	Cd ²⁺	Cu ²⁺	Ni ²⁺	Zn ²⁺
EC ₁	1.67	1.62	0.91	1.22
EC ₂	1.29	1.33	0.89	1.24
PC	0.95	1.31	0.85	0.96
GA	0.82	0.54	0.58	0.53
DW	0.83	0.88	0.99	0.70

capacity of biomass cannot be improved by chemical modifications used in our study. GA has the highest value of $b = 15.7$ L mmol⁻¹ for Cu²⁺, indicating a high affinity for adsorbent. All biosorption capacities of four metals by brown algae are shown in Table 2. The model

Table 3

A comparison of Langmuir, Freundlich and Redlich–Peterson constants q_m (mmol g⁻¹), b (L mmol⁻¹), K , n , K_{RP} (L g⁻¹), α_{RP} (L mol⁻¹) ^{β} , and β resulting from equilibrium uptake studies of four metals by chemically modified and raw brown algae (initial pH between 4.8 and 6.0; s/l ratio 1.0 g L⁻¹; contact time: 180 min)

Models	Sorbent type	Cd ²⁺			Cu ²⁺			Ni ²⁺			Zn ²⁺						
		q_m	b	R^2	q_m	b	R^2	q_m	b	R^2	q_m	b	R^2				
Langmuir	EC ₁	1.85	1.17	0.993	1.78	1.36	0.964	0.98	1.70	0.981	1.42	0.88	0.955				
	EC ₂	1.42	1.42	0.919	1.48	1.27	0.945	1.02	0.98	0.988	1.38	1.28	0.980				
	PC	1.05	1.54	0.922	1.49	0.79	0.986	0.88	2.45	0.989	1.11	1.15	0.979				
	GA	0.67	2.55	0.959	0.41	15.7	0.943	0.26	2.46	0.970	0.62	2.55	0.928				
	DW	0.93	1.52	0.972	0.97	1.39	0.990	1.13	1.25	0.954	0.83	0.74	0.983				
Models	Sorbent type	K	n	R^2	K	n	R^2	K	n	R^2	K	n	R^2				
Freundlich	EC ₁	1.01	3.84	0.956	0.96	0.34	0.976	0.57	3.57	0.953	0.68	3.09	0.971				
	EC ₂	0.93	6.42	0.734	0.82	4.22	0.791	0.51	3.28	0.921	0.71	3.22	0.872				
	PC	0.65	4.94	0.739	0.68	3.22	0.950	0.61	5.56	0.905	0.54	3.05	0.889				
	GA	0.46	2.63	0.943	0.36	5.90	0.948	0.17	3.00	0.992	0.42	3.36	0.768				
	DW	0.57	4.89	0.847	0.56	4.43	0.878	0.63	3.78	0.845	0.36	2.92	0.921				
Models	Sorbent type	K_{RP}	α_{RP}	β	R^2	K_{RP}	α_{RP}	β	R^2	K_{RP}	α_{RP}	β	R^2				
Redlich–Peterson	EC ₁	2.32	1.32	0.98	0.994	6.73	5.73	0.80	0.988	2.26	2.72	0.91	0.987	3.49	4.14	0.76	0.975
	EC ₂	1.38	0.74	1.11	0.953	1.26	0.51	1.23	0.986	0.85	0.70	1.08	0.990	1.48	0.90	1.09	0.984
	PC	1.18	0.86	1.13	0.947	1.28	0.93	0.97	0.987	2.28	2.67	0.99	0.989	1.13	0.91	1.05	0.980
	GA	2.56	4.39	0.85	0.963	12.2	32.0	0.91	0.955	2.63	14.2	0.72	0.994	0.98	1.03	1.41	0.992
	DW	2.23	3.12	0.89	0.954	0.89	1.15	1.02	0.991	2.29	10.3	0.89	0.974	1.68	1.04	0.92	0.985

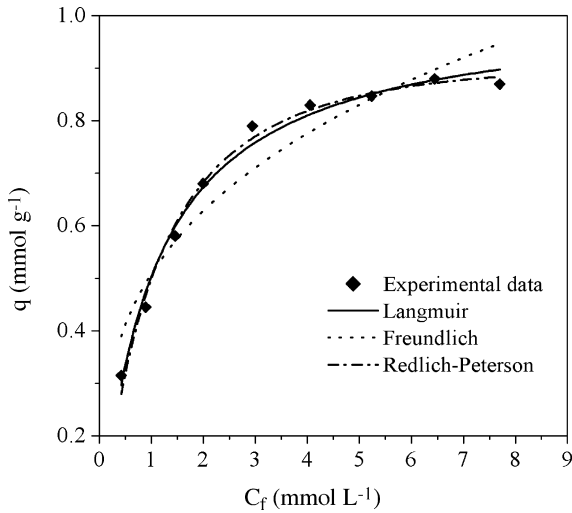


Fig. 3. Fit of the Langmuir, Freundlich and Redlich–Peterson isotherms for nickel biosorption by EC₂ (initial pH 5.0; s/l ratio 1.0 g L⁻¹; contact time: 180 min).

parameters q_m and b resulting from equilibrium uptake studies are listed in Table 3.

The Freundlich expression is an equation based on heterogeneous surfaces suggesting that binding sites are not equivalent

and/or independent. The Freundlich model is described by Eq. (5) [33]:

$$q = KC_f^{1/n} \tag{5}$$

where K and n are the Freundlich constants, the characteristics of the system. K and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The sorption parameters were calculated, and their values together with the correlation coefficients are summarized in Table 3. It is clear that the Freundlich model could not fit all the experimental data well, as R^2 values are generally lower than Langmuir model.

The Redlich–Peterson equation contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms [34]. The Redlich–Peterson isotherm can be described as follows:

$$q = \frac{K_{RP}C_f}{1 + \alpha_{RP}C_f^\beta} \tag{6}$$

where K_{RP} , α_{RP} and β ($0 < \beta < 1$) are the Redlich–Peterson parameters. For $\beta = 1$, the Redlich–Peterson equation converts to Langmuir form. When K_{RP} and α_{RP} are much greater than unity, the equation can transform Freundlich form. The adsorption constants in Table 3 show that the three parameter Redlich–Peterson model describes the adsorption of metal ions better than that of Freundlich model. The equilibrium data were well fit by the Redlich–Peterson isotherm as $R^2 > 0.947$. It can be seen that the values of β are close to

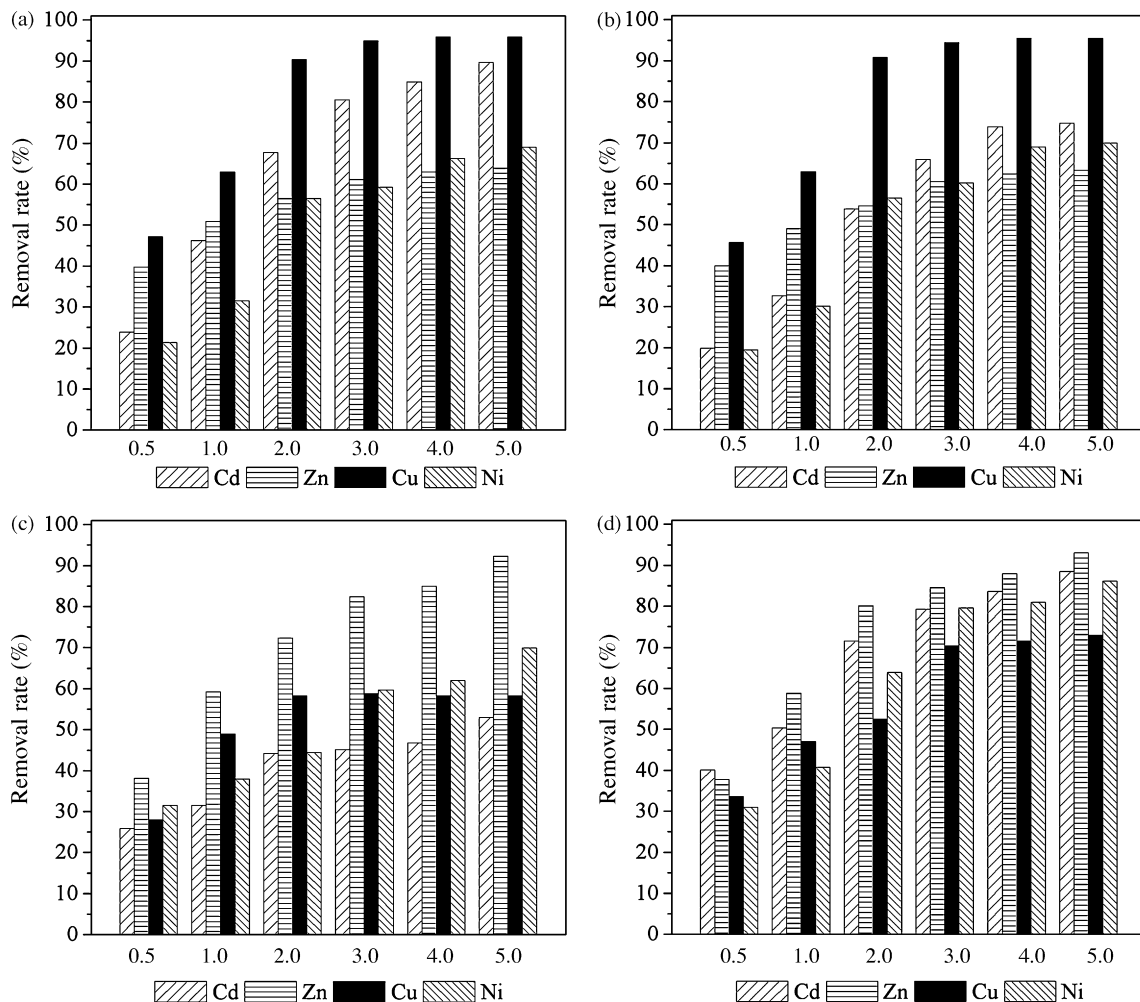


Fig. 4. Effect of s/l ratio on metal biosorption (initial pH 4.8; initial metal concentration 1.0 mmol L⁻¹; contact time: 480 min) by (a) EC₁, (b) EC₂, (c) PC, and (d) DW.

unity, which means that the isotherms are approaching the Langmuir form and not the Freundlich isotherm. Hence, both Langmuir and Redlich–Peterson isotherm models were suitable to fit the experimental data.

Different chemical modifications have been applied to enhance the uptake of metal ions and these methods also can improve the stability and mechanical properties of the algae. In this paper, functional groups responsible for metal ion binding to the algae surface can be changed by these methods. Epichlorohydrin modification is a chemical crosslinking between various polysaccharides via the hydroxylic groups in alkaline conditions. DMSO was used to expose the hidden metal binding groups before crosslinking. The reaction product was washed with diluted 2-propanol to remove excess DMSO and epichlorohydrin. The unique mixture of polysaccharides, mainly alginate and fucoïdan, is largely responsible for the excellent metal sequestering ability of the brown algae [35,36]. In the preparation of EC₁ and EC₂, polysaccharides were crosslinked in strongly basic media using epichlorohydrin in order to prevent their aqueous solubility [37]. As a result, biomass modified by epichlorohydrin has shown a high uptake capacity for metal ions. There are no obvious difference between EC₁ and EC₂. Potassium permanganate was used to oxidize marine brown algae *L. japonica* to increase carboxylic groups, which have been identified as the main metal binding site. Cd²⁺, Cu²⁺ and Zn²⁺ adsorption capacities have been improved by potassium permanganate oxidation. Glutaraldehyde modification resulted in the decrease of metal uptake when compared with the capacities of the raw biomass. It seems that crosslinking of marine algae with glutaraldehyde in particular destroys or changes the metal binding sites. Based on the maximum uptake capacity and cost effect, EC₂ is the best sorbent than EC₁, PC and GA for heavy metal removal applications.

3.4. Effect of solid/liquid ratio on the metal ions adsorption

An important parameter for metal adsorption is the *s/l* ratio defined as the mass of biomass to the volume of the metal solution. For a constant volume of the metal solution (10 mL), different masses of biomass are used: 5, 10, 20, 30, 40 and 50 mg corresponding to *s/l* ratios of 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 g L⁻¹. The effect of *s/l* ratio on metal adsorption is studied at room temperature and at pH 4.8. The initial concentration of the metal solution is 1.0 mmol L⁻¹ and the results are shown in Fig. 4. It is apparent that the four biosorbents have a similar behaviour. At the beginning, the removal rate increases as *s/l* ratio increases. Then the removal rate increases a little when *s/l* ratio above 3.0 g L⁻¹. Thus the optimum *s/l* ratio is 3.0 g L⁻¹ in terms of the cost effect.

4. Conclusions

The pretreated alga has much potential as a biosorbent for the removal of heavy metal ions from wastewaters. Metal uptake capacity increases with time and then reaches equilibrium value about 2 h. The pseudo-first-order kinetic model is in good agreement with all the experimental data compared with the pseudo-second-order kinetic model. The biosorption is pH dependent and the highest uptakes of four metal ions are occurred at initial pH 4.3–6.5 for EC₁, EC₂, PC, GA and DW. The optimum *s/l* ratio is 3.0 g L⁻¹ in terms of the high removal rate and the cost efficiency. EC₁ and EC₂ have shown a high uptake capacity for metals compared with the raw biomass, PC and GA. In terms of metal uptake capacity and cost effect, EC₂ appeared to be an effective and alternative technique for heavy metal removal.

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