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Adsorptive Separation of Metallic Pollutants onto Waste Seaweeds, *Porphyra Yezoensis* and *Ulva Japonica*

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Abstract: From two kinds of seaweeds, *Porphyra yezoensis* and *Ulva japonica*, adsorption gels for heavy metal ions were prepared by enhancing their adsorptive properties and diminishing the aqueous solubility. An environmental benign crosslinking using calcium have shown maximum adsorption capacity of 0.67 mol/kg dry gel for lead(II), which is slightly lower as compared to the adsorbents crosslinked with synthetic crosslinking agent (0.76 mol/kg). Fixed bed column studies for a binary mixture containing lead(II) and zinc(II) revealed that lead(II) can be mutually separated from zinc(II) with a concentration factor of 45.

Keywords: Waste seaweed, ion exchange, adsorption, heavy metals

INTRODUCTION

Large amounts of metals are released into the environment by human activities such as manufacturing processes, smelting and refining, electricity generation, agricultural fertilization, refuse and wastewater treatment, and fuel combustion.

The most commonly practiced treatment for toxic metals includes precipitation as hydroxides or sulfides followed by separation by using suitable coagulating reagents, in some instances, just the coagulation process alone can separate the metals of interest (1, 2). Adsorption onto synthetic

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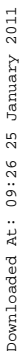
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adsorbents have shown excellent adsorption behavior as compared to the other low-cost adsorbents (25, 27).

EXPERIMENTAL

Preparation of Epichlorohydrin Crosslinked Adsorption Gel

The feed materials for the adsorption gels were dried sheets of *Porphyra yezoensis* waste which were not sold at auctions due to its low quality and *Ulva japonica* collected at the coast of the northern part of Kyushu island, Japan. These seaweeds contain some water soluble components like amino acids and alginic acid. In order to avoid the dissolution in aqueous media, *Ulva japonica* was crosslinked with some different crosslinking agents, epichlorohydrin, formaldehyde, and calcium, to compare the effects of crosslinking agents using the same procedures adopted in our previous studies (26, 28). In the case of crosslinking with epichlorohydrin in particular, both *Porphyra yezoensis* and *Ulva japonica* were crosslinked under the same condition for comparison.

The feed materials were crushed into powder using a Daltons type II power mill. 20 g of powder was mixed together with 150 mL of dimethylsulfoxide in a 500 mL round bottom flask and stirred overnight at a speed of 200 rpm at 30°C. Then, 20 mL of epichlorohydrin was added and stirred for 2 h at 50°C. Further, 25 mL of 5M ($M = \text{mol dm}^{-3}$) sodium hydroxide solution was added and stirred for 5 h. The suspension was cooled down to room temperature and filtered. The solid residue obtained after filtration was washed with 70% propanol solution until the filtrate became neutral. It was further washed with 0.5 M hydrochloric acid solution followed by again with 70% aqueous propanol to neutrality. It was dried in a convection oven for 24 h at 70°C and finally grounded into powder to pass the mesh size of 200 μm .

Preparation of *Ulva Japonica* Gel Crosslinked with Formaldehyde

20 g of dried powder of *Ulva japonica* was taken in a 500 mL beaker in which it was mixed together with 0.5 mL of 12 M hydrochloric acid, 99.5 mL 35% of formaldehyde and 120 mL of pure water and stirred for 2 h. The mixture suspension was centrifuged to make the phase separation between solids and liquid. The resultant solid was dried at 70°C in a convection oven. The dried product was washed with 0.1 M sodium hydroxide solution, filtered, and washed with 70(v/v)% propanol followed by washing with 0.5 M hydrochloric acid, then with 70% propanol till neutralization. The washed and filtered product was dried in a convection oven at 70°C. After drying, the material was grounded into fine powder and sieved to pass the mesh size of

200 μm . The yield of the final product, fine yellow brown dried and powdered crosslinked product, was 7.8 g.

Preparation of *Ulva Japonica* Gel Crosslinked with Calcium

20 g of dried *Ulva japonica* powder and 500 mL of 0.32 M calcium chloride were mixed in a 1000 mL round bottom flask and stirred for 24 h. The suspension was filtered and the solid product was washed with 70(v/v)% propanol and kept for drying in a convection oven for 24 h at 70°C. The dried powder was made into fine powder to pass the mesh size of 200 μm . 6.76 g dark green powder of calcium-crosslinked product was obtained.

Adsorption Studies

Aqueous solutions of 15 mg/L of lead(II), cadmium(II), copper(II), zinc(II), nickel(II), aluminum(III), iron(III), lanthanum(III), and cerium(III) were prepared by dissolving corresponding analytical grade metal chloride or nitrate salts into 0.1 M nitric acid and 0.1 M 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulphonic acid (HEPES) buffer solution, respectively. These two solutions were mixed at an arbitrary ratio to adjust pH.

In the batchwise tests, 20 mg of the dried adsorbent was taken in the 50 mL conical flask together with 15 mL of corresponding aqueous solution. The flask was shaken vigorously in a thermostated shaker at 30°C for about 24 h at 150 rpm to attain equilibrium. The initial and equilibrium concentrations of metal ions were measured by using a Shimadzu Model ICPS-8100 ICP/AES spectrometer or a Shimadzu AA-6650 atomic absorption spectrophotometer. The adsorption efficiency, A%, of the metal ion was calculated by

$$A\% = (C_i - C_e)/C_i \times 100 \quad (1)$$

The sorption capacity of metal ions is the concentration of metal ions on the adsorbent and is calculated based on the mass balance principle as,

$$q = \{(C_i - C_e)/W\} \times (L/1000) \quad (2)$$

In the above equations, q represents the amount of metal uptaken per unit mass of the adsorbent (mol kg^{-1}), L the volume of the test solution (mL), W the dry mass of the adsorbent (kg), C_i , and C_e the initial and final concentrations (mol dm^{-3}), respectively.

The mutual adsorptive separation of lead(II) from zinc(II) was carried out using a glass column of 8 mm internal diameter packed with 0.1 g of epichlorohydrin crosslinked *Ulva japonica* gel. The column was conditioned by passing water of pH = 4.5 overnight prior to the adsorption of metal ions. The sample solution containing 20 mg/L of lead(II) and 200 mg/L of

zinc(II) whose pH was maintained at 4.5 was percolated into the column at a constant flow rate of 3.31 mL/h using a peristaltic pump (IWAKI PST-100N, Japan). Effluent samples were collected at each one-hour interval of time by using a fraction collector (BIORAD Model 2110 Fraction Collector) to measure the corresponding metal ion concentrations.

For the elution tests, the column was pre-washed with deionized distilled water so as to expel any unbounded metal ions by physical adsorption. 0.1 M nitric acid solution used as the eluent was percolated into the column at the same constant flow rate of 3.31 mL/h using the peristaltic pump. The concentration of the eluted metal ions collected at each interval in the tube of fraction collector was measured by using a Shimadzu Model ICPS-8100 ICP/AES spectrometer.

Evaluation of Exchangeable Protons

The evaluation of the exchangeable protons from alginic acid contained in *Porphyra yezoensis* and *Ulva japonica* before/after crosslinking was carried out as follows. 50 mg of dried gel and 30 ml of 0.01 N of sodium hydroxide was taken into five separate stoppered bottles for each sample and shaken for 24 h at a temperature of 30°C. The decrease in basicity was evaluated by titrating the filtrate with standardized 0.01 hydrochloric acid using phenolphthalein as the indicator. In the case of the calcium-crosslinked *Ulva Japonica*, 20 mg of gel was equilibrated with 15 mL of 0.5 M of nitric acid for 24 h at 30°C. The concentration of calcium leached out in the filtrate was measured by atomic absorption spectrometer (AAS).

Solubility of *Porphyra yezoensis* and *Ulva japonica* into Aqueous Solution

The dissolution of the alginic acid in *Porphyra yezoensis* and *Ulva japonica* can be suppressed by crosslinking and water soluble low molecular weight components such as amino acids are removed during the several steps of washing described above. However, there is a possibility that a small amount of water soluble components may still exist in the gel and can be dissolved into the aqueous solutions during the adsorption, which not only increases BOD and COD in the solution but also may impede the adsorption of metal ions. In order to assess such possibility, the total organic carbon (TOC) concentration in water contacted with the crosslinked and non-crosslinked powder was measured as follows. Dried 0.15 g of dried gels were equilibrated with 15 ml of distilled water at pH = 1.6, 3.0, 5.07, 5.99, and 7.19, respectively, by shaking at 30°C for 48 h in a thermostated air bath. It was then filtered and the subsequent pH and TOC concentration of

the filtrate was measured by using a BECKMAN model $\Phi 45$ pH meter and a Shimadzu model TOC-VSH TOC analyzer, respectively.

RESULTS AND DISCUSSION

Evaluation of Exchangeable Cations

The amount of exchangeable protons contained in uncrosslinked *Porphyra yezoensis* and *Ulva japonica* was evaluated as 0.96 and 1.98 mol/kg dry gel, and, while it was 0.60 and 1.52 mol/kg after crosslinking, respectively. A similar analysis indicated 3.65 mol/kg of exchangeable protons in the case of pure non-crosslinked alginic acid. On the other hand, the amount of calcium released from the calcium-cross linked *Ulva japonica* gel was 1.03 mol/kg dry gel. The experimental observation concludes that a much cheaper adsorbent having the same functional analog could be prepared for the purpose of removing toxic heavy metals by the application of seaweeds.

Aqueous Solubility of *Porphyra Yezoensis* and *Ulva Japonica* Seaweeds

Figure 1 shows the dissolution of crosslinked and non-crosslinked *Porphyra yezoensis* and *Ulva japonica* gels as a measure of total organic carbon (TOC) concentration at varying pH. It is seen that dissolution of the non-crosslinked gel is quite significant with the increase in pH, while it is greatly suppressed

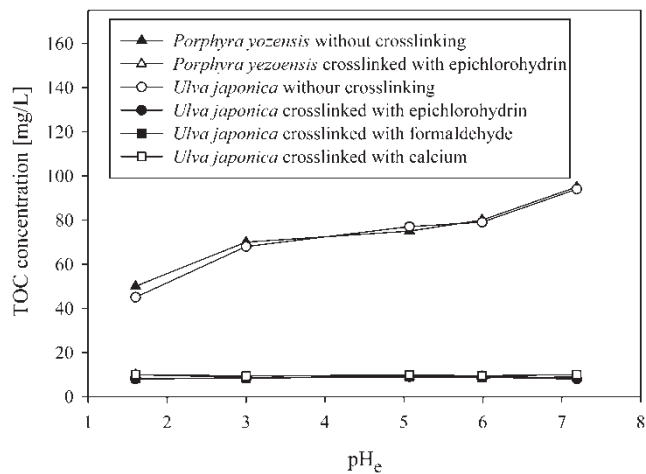


Figure 1. Dissolution of non-crosslinked and crosslinked *Porphyra yezoensis* and *Ulva japonica* as a measure of TOC concentration at a solid to liquid ratio of 10 g/L.

in the cases of crosslinked gels. The partial solubility of the gel may be attributable to the dissolution of some water soluble organic acids such as amino acids. The dissolution from the crosslinked gels was less than 10 mg/L indicating that the effluent TOC concentration appeared to meet the environmental regulations.

Adsorption Behavior of Epichlorohydrin Crosslinked *Porphyra Yezoensis* and *Ulva Japonica*

Figures 2 and 3 shows the % adsorption of lead(II), cadmium(II), copper(II), zinc(II), nickel(II), iron(III), aluminum(III), lanthanum(III), and cerium(III) ions onto epichlorohydrin-crosslinked *Porphyra yezoensis* and *Ulva japonica* gels, as the function of equilibrium pH. As seen from these figures, the adsorption of the metal ions on both gels increases with the increase in pH, suggesting that metal ions are adsorbed according to a cation exchange mechanism, releasing protons from the carboxyl analog of the alginic acid contained in the gel as expected from the previous work on the alginic acid gel. This is further supported by the fact that the pH of the aqueous solution had been decreased after the adsorption of metal ions. Although lead(II) and iron(III) can be quantitatively adsorbed onto the *Porphyra yezoensis* gel, the adsorption behavior of *Ulva japonica* gel seems far better than *Porphyra yezoensis* gel, since the % adsorption of all metal ions tested are higher under the same experimental conditions. It has been further confirmed by the adsorption of lead(II) and zinc(II) from its corresponding binary mixture onto *Ulva japonica* and *Porphyra yezoensis* gels,

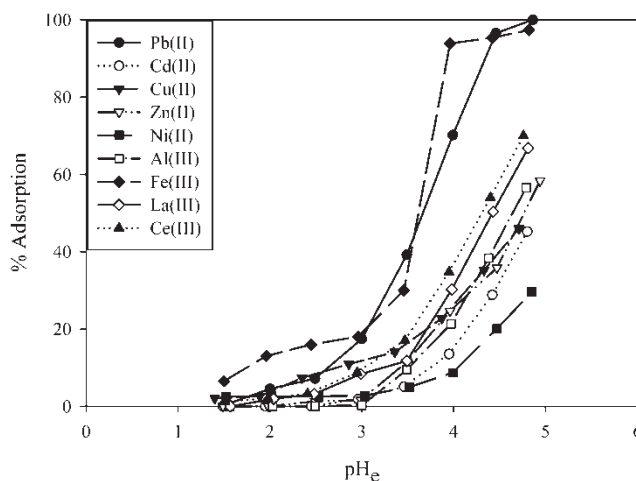


Figure 2. Effect of pH on adsorption of several metal ions onto *Porphyra yezoensis* gel crosslinked with epichlorohydrin. Weight of the gel = 20 mg. Volume of the aqueous solution = 15 mL. Initial metal concentration = 15 mg/L.

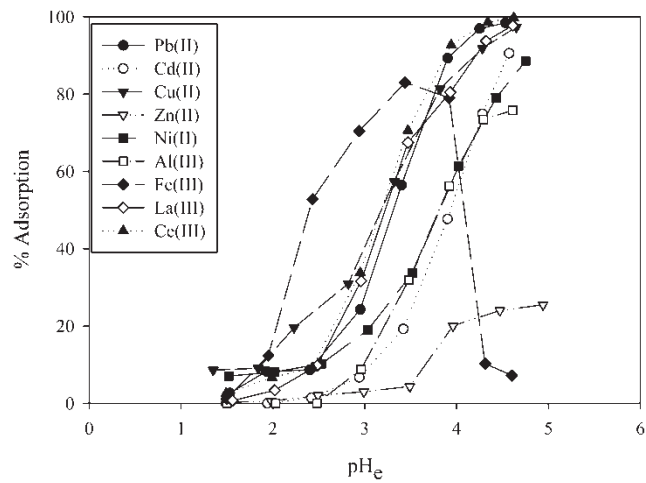


Figure 3. Effect of pH on adsorption of several metal ions onto *Ulva japonica* crosslinked with epichlorohydrin. Weight of the gel = 20 mg. Volume of the aqueous solution = 15 mL. Initial metal concentration = 15 mg/L.

where separation factors for lead(II) over zinc(II) observed to be higher in the case of former compared with the latter gel as shown in Fig. 4.

Figures 5 and 6 show adsorption isotherms of lead(II), cadmium(II), copper(II), lanthanum(III), and cerium(III) on the gels of *Porphyra yezoensis* and *Ulva japonica*, respectively. The adsorption isotherms of both

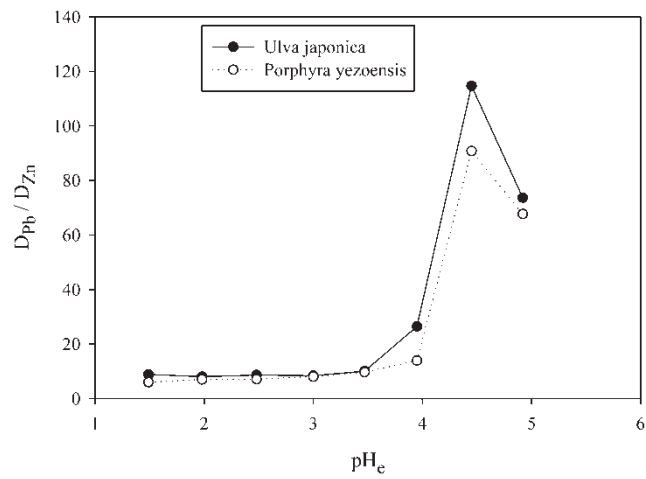


Figure 4. Separation factor for Pb(II) over Zn(II) at identical conditions onto *Ulva japonica* and *Porphyra yezoensis* crosslinked with epichlorohydrin. Initial concentration of Pb(II) and Zn(II) was 15 mg/L in the binary mixture solution, weight of the gel = 20 mg, and volume of the metal solution = 15 mL.

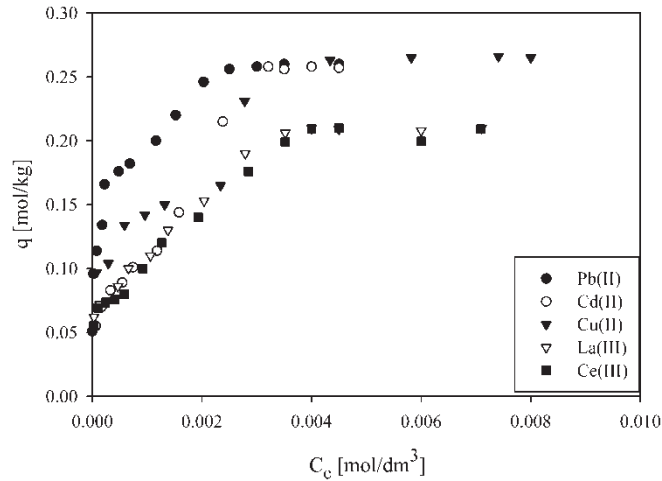


Figure 5. Adsorption isotherms of some metal ions on epichlorohydrin crosslinked *Porphyra yezoensis* gel. Weight of the gel = 20 mg. Volume of the aqueous solution = 15 mL at pH ~5.0.

gels exhibit Langmuir type adsorption for all metals tested; i. e. the adsorption increases with increasing metal concentration in the low concentration region and tends to approach constant values corresponding to each metal ions, from which maximum adsorption capacities were evaluated.

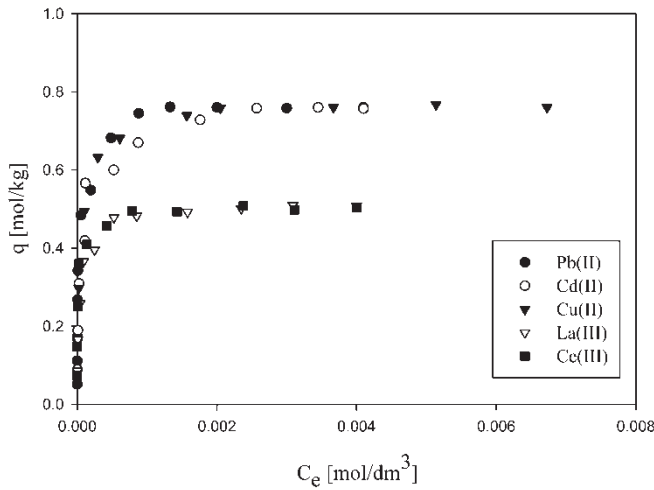


Figure 6. Adsorption isotherms of some metal ions onto epichlorohydrin cross-linked *Ulva japonica* gel. Weight of the gel = 20 mg. Volume of the aqueous solution = 15 mL at pH ~5.0.

Those on *Porphyra yezoensis* gel were evaluated as 0.26 mol/kg dry gel for all of the three kinds of divalent metal ions, while for the other two kinds of trivalent metal ions, they were 0.21 mol/kg. Similarly, in the case of *Ulva japonica* gel, they were evaluated as 0.76 and 0.51 mol/kg dry gel for divalent and trivalent metal ions, respectively

$$C_{eq}/q = C_{eq}/Q_{max} + 1/b \cdot Q_{max} \tag{3}$$

Figure 7 shows the plot according to Eqn. (3), the well-known Langmuir equation, for the adsorption on *Ulva japonica* gel. A similar plot was obtained also for *Porphyra yezoensis* gel. Tables 1(a) and (b) lists the Langmuir parameters, Q_{max} and b , together with the maximum adsorption capacities evaluated from Figs. 5 and 6. Since the adsorption properties of *Ulva japonica* gel was found to be much better than *Porphyra yezoensis* gel, subsequent studies were carried out on the former.

Effect of Crosslinking Agents

We observed that the maximum adsorption capacities for all divalent metal ions tested were the same values in the unit of mol/kg- dry gel and similar trend was observed for the trivalent metals as mentioned in the previous section. Under such circumstances, the effect of crosslinking agents on the adsorption was examined for lead(II) and copper(II) as the representative divalent metal ions while cerium(III) as the trivalent metal. Fig. 8 shows the % adsorption of these metal ions as the function of pH on *Ulva japonica* gel crosslinked with formaldehyde while % adsorption on the *Ulva japonica* gel crosslinked with calcium is shown in Fig. 9. Interestingly, cerium(III) is

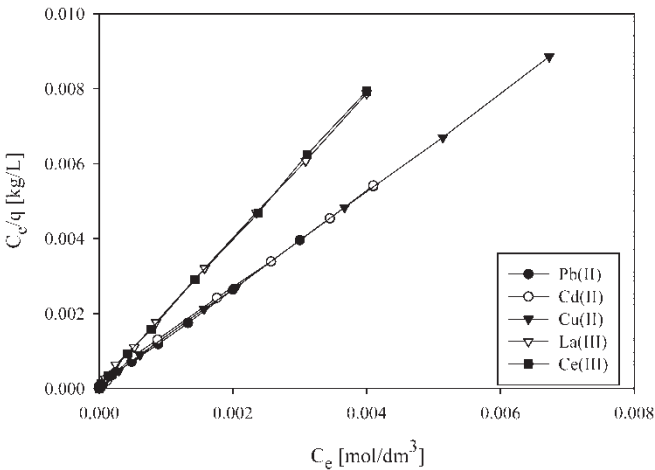


Figure 7. Langmuir plot for the adsorption of some metal ions onto *Ulva japonica* at 30°C.

Table 1(a). Langmuir adsorption isotherm model parameters and experimental Q_{\max} for *Ulva japonica* gel

Metal	Q_{\max} [mol/kg] Langmuir model	Q_{\max} [mol/kg] Experimental	b [dm ³ /mol]	R ²
Pb(II)	0.77	0.76	4.4×10^4	0.99
Cd(II)	0.77	0.76	14×10^4	0.99
Cu(II)	0.77	0.76	2.1×10^4	0.99
La(III)	0.51	0.51	2.4×10^4	0.99
Ce(III)	0.50	0.51	6.6×10^4	0.99

Table 1(b). Langmuir adsorption isotherm model parameters and experimental Q_{\max} for *Porphyra yezoensis* gel

Metal	Q_{\max} [mol/kg] Langmuir model	Q_{\max} [mol/kg] Experimental	b [dm ³ /mol]	R ²
Pb(II)	0.27	0.26	5.3×10^3	0.99
Cd(II)	0.32	0.26	0.8×10^3	0.90
Cu(II)	0.29	0.26	1.2×10^3	0.98
La(III)	0.23	0.21	15×10^3	0.98
Ce(III)	0.23	0.21	13×10^3	0.98

selectively adsorbed over lead(II) on the latter gel, while it was the same with the cerium(III) in the case of the former gel. The adsorption of copper(II) was remarkably decreased on the latter gel under the same experimental conditions. This may be attributable to relatively easy dissolution of calcium at low pH where the adsorption of cerium(III) is predominant over the other metal ions tested.

Although crosslinking of solid adsorbents avoids their aqueous solubility, it decreases the number of sites available for ion exchange adsorption and vice versa. In order to assess a suitable crosslinking agent and effective adsorption behavior, the adsorption isotherms of lead(II) on *Ulva japonica* gel crosslinked with three different kinds of agents mentioned earlier were compared as shown in Fig. 10. It can be seen that epichlorohydrin and formaldehyde crosslinked gel had exhibited the same adsorption capacity of 0.76 mol/kg of dry gel, while that of the calcium crosslinked gel was 0.67 mol/kg dry gel, both of which are much higher than macroalga, activated carbon, peanut hulls, and cornstarch corresponding to 0.138, 0.147, 0.145, and 0.139 mol/kg adsorbent, respectively (25, 27). In the previous paper (28), we reported that the maximum adsorption capacity of lead(II) onto pure alginic acid gel crosslinked with epichlorohydrin was 1.2 mol/kg, which is higher than those exhibited by the gel of *Ulva japonica*. However, the values of 0.76 or 0.67 mol/kg can be appreciated to be a quite reasonable adsorption capacity taking into consideration that these adsorption gels can be prepared at comparatively cheaper cost.

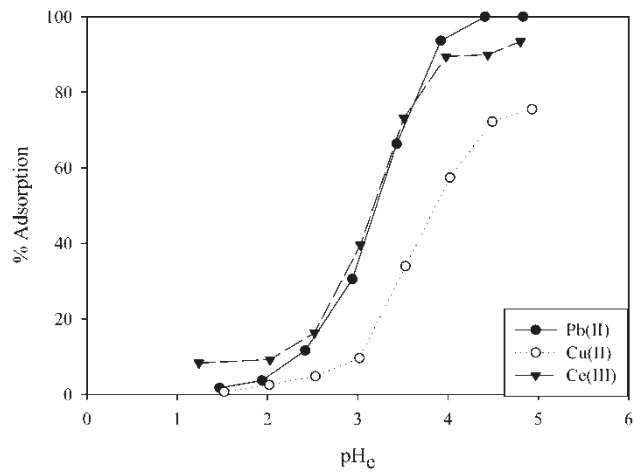


Figure 8. Effect of pH on adsorption of some metal ions on formaldehyde crosslinked *Ulva japonica* gel. Weight of the gel = 20 mg. Volume of the aqueous solution = 15 mL. Initial metal concentration = 15 mg/L.

Separation of Binary Metal Ion Mixture by Column

Figure 11 shows the breakthrough curves of lead(II) and zinc(II) from the column packed with epichlorohydrin crosslinked *Ulva japonica* gel at an

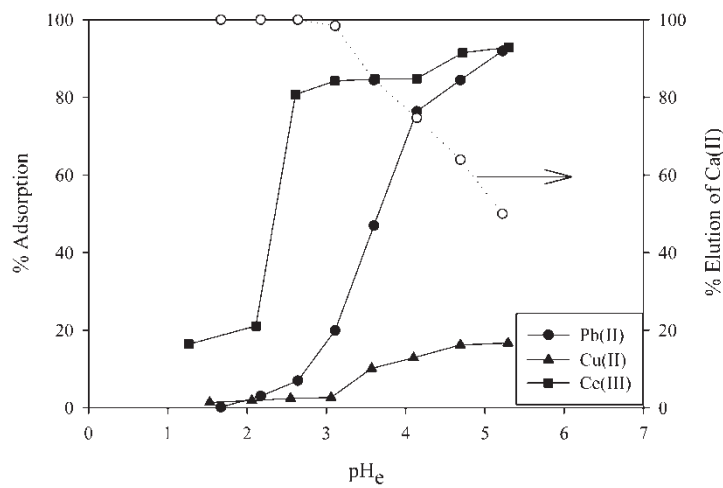


Figure 9. Effect of pH on adsorption of some metal ions on calcium crosslinked *Ulva japonica* gel and subsequent elution of calcium(II) in the solution. Weight of the gel = 20 mg. Volume of the aqueous solution = 15 mL. Initial metal concentration = 15 mg/L.

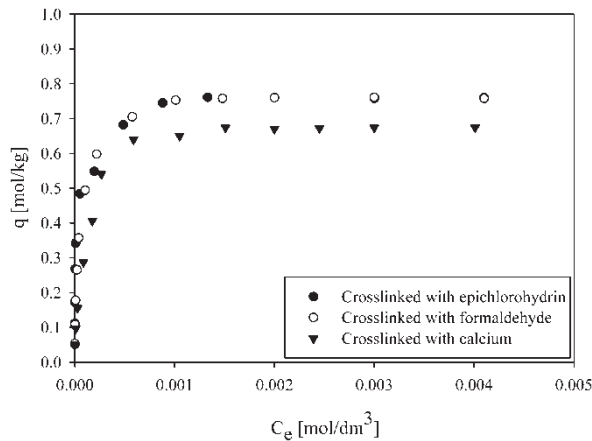


Figure 10. Adsorption isotherm of lead(II) on three different types of crosslinked *Ulva japonica* gel. Weight of the gel = 20 mg. Volume of the aqueous solution = 15 mL at their optimum pH ~5.0.

initial concentration of 10 and 200 mg/L, respectively. This figure shows that the breakthrough of lead(II) occurred at 907 bed volumes while that of zinc(II) took place at 50 bed volumes, suggesting very easy mutual separation between these metal ions by using the packed column, which is attributable to the high selectivity to lead(II) over zinc(II) as mentioned

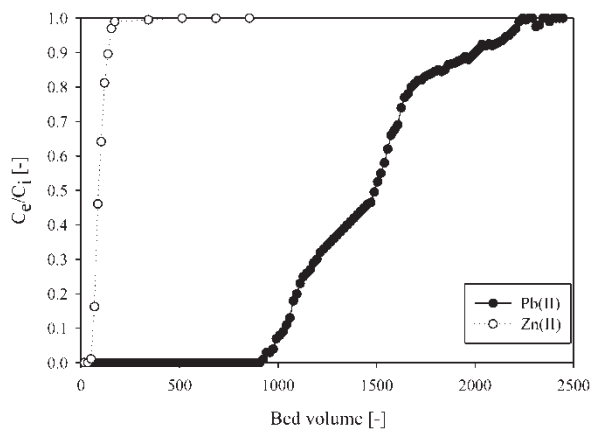


Figure 11. Breakthrough curve of lead(II) and zinc(II) from the column packed with epichlorohydrin crosslinked *Ulva japonica* gel at an initial concentration of 20 and 200 mg/l, respectively. The pH of the solution was maintained at 4.5 with a flow rate of 3.31 ml/h, while the dry weight of the packed gel was 100 mg. Bed volume = aqueous solution passed through the column/volume of packed gel. C_e : effluent concentration, C_i : feed concentration.

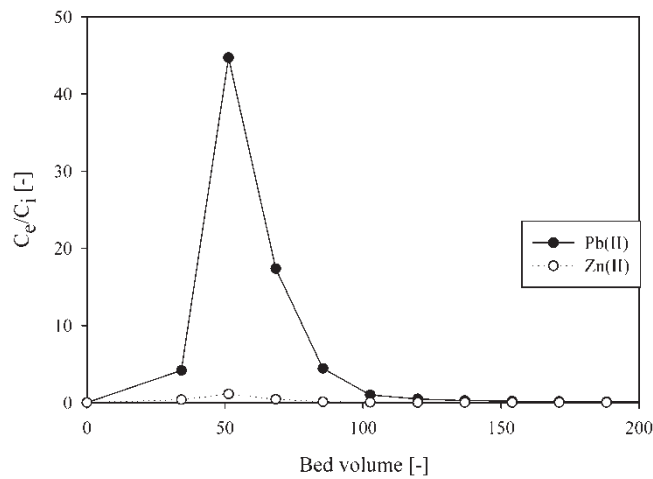


Figure 12. Elution profile of lead(II) and zinc(II) from the column using 0.1 M nitric acid. Bed volume = aqueous solution passed through the column/volume of packed gel. C_e : effluent concentration, C_i : feed concentration in the breakthrough test.

earlier. The amount of lead(II) adsorbed onto the gel packed in the column was evaluated to be 5.2 mg/100 mg gel, which is equivalent to 0.25 mol/kg dry gel. The loading capacity evaluated from the column experiment is lower than that evaluated in the batchwise adsorption test, which can be reasonably attributed to the fact that the space velocity of the metal solution tends to have a little time for equilibration. The adsorbed lead ion was completely eluted at 150 bed volumes by using 0.1 M nitric acid solution while only negligible concentration of zinc was detected in the effluent, as seen in Fig. 12. The lead(II) eluted from the column based on Fig. 12 was 5.1 mg, while that adsorbed was 5.2 mg in accordance to the breakthrough curve as mentioned in Fig. 11, suggesting that 98.3% of lead(II) was recovered. Thus the present adsorbent is quite efficient for the separation into its individual components of lead(II) and zinc(II) from their binary mixture.

CONCLUSIONS

Adsorptive separation of several metal ions on two kinds of waste seaweeds *Porphyra yezoensis* and *Ulva japonica* have been investigated using different crosslinking agents. Irrespective of the synthetic crosslinking agents employed like epichlorohydrin and formaldehyde, the crosslinked gel obtained from *Ulva japonica* had exhibited better performance with regard to the selectivity and maximum adsorption capacity in the adsorption of divalent and trivalent metal ions from aqueous media compared with the gel

prepared from *Porphyra yezoensis*. But the calcium crosslinked gel exhibited a higher selective nature for higher valent metal ion like cerium(III).

The maximum adsorption capacity of lead(II) evaluated for the *Ulva japonica* gel crosslinked with synthetic crosslinking agent like epichlorohydrin and formaldehyde was 0.76 mol/kg dry gel, while it was 0.67 mol/kg for the gel crosslinked with calcium. The maximum adsorption capacity of the seaweeds and the amount of their respective exchangeable cations evaluated by titration or calcium determination from the calcium cross-linked seaweed are in close agreement. Although the calcium crosslinked gel had a little bit lower adsorption capacity, it is environmentally benign material as it is free from the synthetic chemical reagents and it still possesses much higher maximum adsorption values for lead(II) than other adsorbents so far reported like macroalga, activated carbon, peanut hulls, and cornstarch.

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