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# Biosorption of copper by immobilized marine algal biomass

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**Abstract**

The characteristics of poly(vinyl alcohol) (PVA) cryogel as an immobilization matrix were examined for the uptake of copper by a brown marine algal biomass, and compared with freely suspended biomass. Biomass-embedded PVA cryogel beads were robust and showed stability under a wide range of pH (1–13). SEM analysis revealed the rugged surface of the beads and changes in its surface compositions before and after metal binding. The surface area and pore size of the beads were highly dependent on the concentration of the biomass immobilized within the PVA beads. The immobilized beads showed lower copper uptake capacity than the freely suspended *Sargassum*. A positive correlation was also found between copper uptake capacity and the concentration of the immobilized biomass (5–30 g/L). The metal uptake capacity of the beads was also dependent on the solution pH. It was shown that immobilization matrix exerted mass transfer resistance for copper uptake by the PVA-*Sargassum* beads. The metal sorption rates were enhanced at higher biomass loading within the beads, or with an increase in the initial copper concentration, or with hydration of the beads before use. The kinetics of copper biosorption by the immobilized PVA cryogel bead could be well modeled by a pseudo first-order equation.
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*Keywords:* Biosorption; Poly(vinyl alcohol) cryogel; *Sargassum*; Copper

## 1. Introduction

Biosorption is essentially the passive and physicochemical binding of metal ions to chemical sites naturally present in a biomass. The non-viable form of the biomass has been proposed as a potential biosorbent over living biomass since the former is a dead material which requires no nutrients, and problems associated with metal toxicity in living biomass and the need to provide suitable growth condition also do not arise [1]. Biosorption could be employed most effectively in aqueous solutions with pollutants present at trace concentrations (typically below 100 mg/L) and where conventional physical and chemical treatment methods are either ineffective or costly [2,3].

Various biomass of microbial, fungal, algal or crustacean origin have been investigated as biosorbent materials. In particular, many studies have focused on marine algae due to its easy availability and high uptake capacity [2,3]. Indeed, a few brown algae showed much higher uptake capacity than that of activated carbon, natural zeolites and synthetic ion exchange resins [4].

Unfortunately, free algal cells are not suitable for use as a column packing since the cells tend to clump together and excessive hydrostatic pressure are required in order to generate suitable flow rates. Furthermore, since the algal cells are inherently fragile, high pressure may cause disintegration of the free biomass. The fragility problem has been alleviated by the immobilization of the algae within a suitable porous matrix. Amongst the various immobilization methods, entrapment (whereby the biomass is enclosed within a polymeric matrix) is one of the most commonly used methods. Poly(acrylamide) gel, calcium alginate gel and poly(vinyl alcohol) (PVA) cryogel are among the porous matrices that have been used to immobilize non-viable algae and to permit their use in packed columns for metal ion recovery.

Poly(acrylamide) gel was the first polymer used for cell entrapment, but the free radicals generated in the course of polymerization were found to be toxic to both microorganisms and humans [5]. The gels prepared from natural polysaccharides such as alginates, $\kappa$-carrageenan and agarose are commonly used in cell immobilization [6]. These natural hydrogels unfortunately abrade easily [7] or dissolve in the presence of competitive ions [8], thus limiting their application under actual process effluent conditions. The use of poly(vinyl alcohol) gel as a matrix for cell immobilization has been extensively studied in various biological systems. PVA cryogel offers various advantages over

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the conventional alginate hydrogels including low cost, high durability and chemical stability, and non-toxicity to viable cells [9].

This work examines the use of PVA gel as an immobilization matrix for the uptake of copper by *Sargassum* sp. The beads were first characterized using SEM and BET analysis. The robustness and stability of the PVA cryogel beads were also investigated. A series of experiments was then carried out to study the effect of physicochemical conditions on the biosorption of copper by the immobilized PVA cryogel beads.

## 2. Materials and methods

### 2.1. Chemicals and biomass

Copper nitrate was obtained from Merck (Germany). Poly(vinyl alcohol) (average molecular weight 72,000 Da) was purchased from FLUKA. All chemicals are of analytical reagent grade. A 0.1 M hydrochloric acid and 0.1 M sodium hydroxide were prepared for pH adjustment.

The raw biomass of *Sargassum* sp. was harvested from the coasts in Singapore. The biomass were washed with deionized water to remove extraneous materials and dried overnight at 60 °C. The dried biomass was then ground to various particle sizes and stored before use.

### 2.2. Immobilization

Blank PVA cryogel beads were fabricated using the iterative freeze–thaw–freeze method [10,13,14]. Firstly, 10 g of PVA was dissolved in 100 mL deionized water and stirred with a magnetic stirrer at 80 °C. During the dissolution, the solution volume was maintained at 100 mL by adding deionized water. After all the PVA had been dissolved, the polymer solution was cooled to room temperature and continuously stirred for 12–16 h to ensure a uniform solution. The resulting 10% PVA solution was transferred to an extrusion contraption by a peristaltic pump at very low flow rate (<5 mL/min) and introduced dropwise into liquid nitrogen, with a longitudinal coaxial air flow to control the bead size. The needle size used was 19 G (1.1 mm). The frozen beads were then placed in a freezer with temperature held at approximately −20 °C for 1–2 h. Next, all the beads were transferred to a refrigerator to be thawed at 4 °C. When all the beads have regained their characteristic elastic behavior, they were contacted with liquid nitrogen again. This freeze–thaw–freeze cycle was repeated twice (i.e., a total of three cycles). The beads were finally left in a dessicator for several days and periodically taken out for weight measurement. The beads were ready for experimental use only when consecutive measurements indicated no change in weight.

Biomass in the size range 65–212 μm was immobilized within PVA cryogel beads in the same manner as that for the blank PVA cryogel beads, except that the biomass was thoroughly mixed with the PVA solution before extrusion. Few batches of biomass-loaded beads of different biomass concentration (5 g dry biomass/L PVA solution, 10, 20, 30 g/L) were fabricated. The resulting *Sargassum*-immobilized PVA cryogel beads were referred to 5, 10, 20 and 30 g/L PVA-*Sargassum* beads, respectively. In this study, the PVA-biomass solution in excess of 30 g/L biomass concentration was too viscous for the experimental apparatus used; the concentrated solution often clogged the hollow needle used for extrusion.

### 2.3. Metal biosorption experiments

The pH of the metal solutions in the conical flasks was first adjusted to the desired values by using 0.1 mol/L $HNO_3$ or NaOH; the sorbent was then added into the solutions while stirred at 200 rpm at room temperature (22 ± 1 °C). The pH was measured at 20–30 min interval and adjusted accordingly. The supernatant samples for kinetics experiments were taken at periodic time intervals. For pH effect and isotherm experiments, the flasks were agitated until the pH was stable for more than 3 h. The supernatant taken during experiments was acidified and filtered (0.45 μm), and the metal concentrations were measured by an inductively couple plasma optical emission spectrometer (ICP-OES) (Perkin-Elmer Optima 3000). The metal uptake was calculated using the following equation:

$$q = \frac{V(C_i - C_f)}{W} \quad (1)$$

where $q$ is the metal uptake, $V$ the solution volume, $W$ the amount of biomass, and $C_i$ and $C_f$ are the initial and the final (or equilibrium) metal concentrations, respectively.

All experiments in this work were conducted in duplicate and the average results were presented.

### 2.4. Abrasion test

A 2 g of blank or biomass-loaded PVA cryogel beads were stirred in 1.0 L deionized water at 400–500 rpm. Fifty beads were randomly taken before and after stirring, and their diameters and weights were measured with a digital micrometer caliper (Mitutoyo 323) and a digital balance (Mettler Toledo B204-S), and the results were analyzed to establish the robustness of the beads.

### 2.5. Chemical stability

Using 0.1 M hydrochloric acid and sodium hydroxide, solutions of pH from 1 to 13 were prepared. The beads were soaked and stirred at 150 rpm for 72 h after which 50 beads were removed, thoroughly rinsed with deionized water and dried, before the weight was measured.

### 2.6. Scanning electron microscopy

The beads were visualized using a scanning electronic microscope (JEOL, JSM-5600 V, Japan) in order to directly observe the surface microstructures of the bead at different forms. SEM requires an ion coating with platinum by a sputter coater (JEOL, JFC-1300, Japan) for 40 s in a vacuum at a current intensity of 40 mA after preparing the sample on metallic studs with double-sided conductive tape.

## 3. Results and discussion

### 3.1. Characterization of PVA cryogel beads

Samples of blank and biomass-immobilized PVA cryogel beads were observed using SEM with the aim to identify the surface microstructures and determine the chemical composition. The SEM images of the beads in Fig. 1a–c showed the absence of pore development within the beads. The cross-sectional image of the PVA-*Sargassum* in Fig. 1a shows the approximate dimensions of the bead and the biomass embedded within. The morphology of surface matrix of the PVA-*Sargassum* beads before and after copper binding, shown in Fig. 1b and c, revealed that the bead surface became less rugged after metal binding.

The surface area and pore size of the blank and seaweed-immobilized beads were measured using BET analysis with nitrogen as the adsorbate. The surface area of blank beads was 8.13 $m^2$/g (see Table 1), and immobilization of the biomass led to a significant decrease in the surface area. The pore size of the beads were also affected; the pore size of blank beads was about 34.76 Å, and increased to 108.20 and 146.12 Å for 10 and 30 g/L PVA-*Sargassum* beads, respectively. The changes in surface area and pore size are the result of several physicochemical factors. It is speculated that water is entrapped within the biomass; the cryogels with higher biomass loading thus contained relatively larger amount of water. Evaporation of water from the beads would result in a larger pore size and smaller surface area. A surface area of 3.40–5.63 $m^2$/g has been reported for biomass-immobilized polysulfone beads [11,12]. Since the surface and pore structure of the beads are strongly affected by the properties of support matrix, the biomass and its dosage, as well as its processing conditions, direct comparison is difficult although the values are not very dissimilar.

Table 1
Physical properties of blank and PVA-*Sarsassum* beads

| | Blank | PVA-*Sargassum* beads | |
|---|---|---|---|
| | | 10 g/L | 30 g/L |
| BET surface area ($N_2$) ($m^2$/g) | 8.13 | 1.71 | 0.15 |
| Average pore sizes (Å) | 34.76 | 108.20 | 146.12 |

### 3.2. Robustness and stability of PVA cryogel beads

PVA cryogel beads were highly elastic. It has been reported that the PVA cryogel beads did not fracture under a compressive force of up to 2.5 N [13].

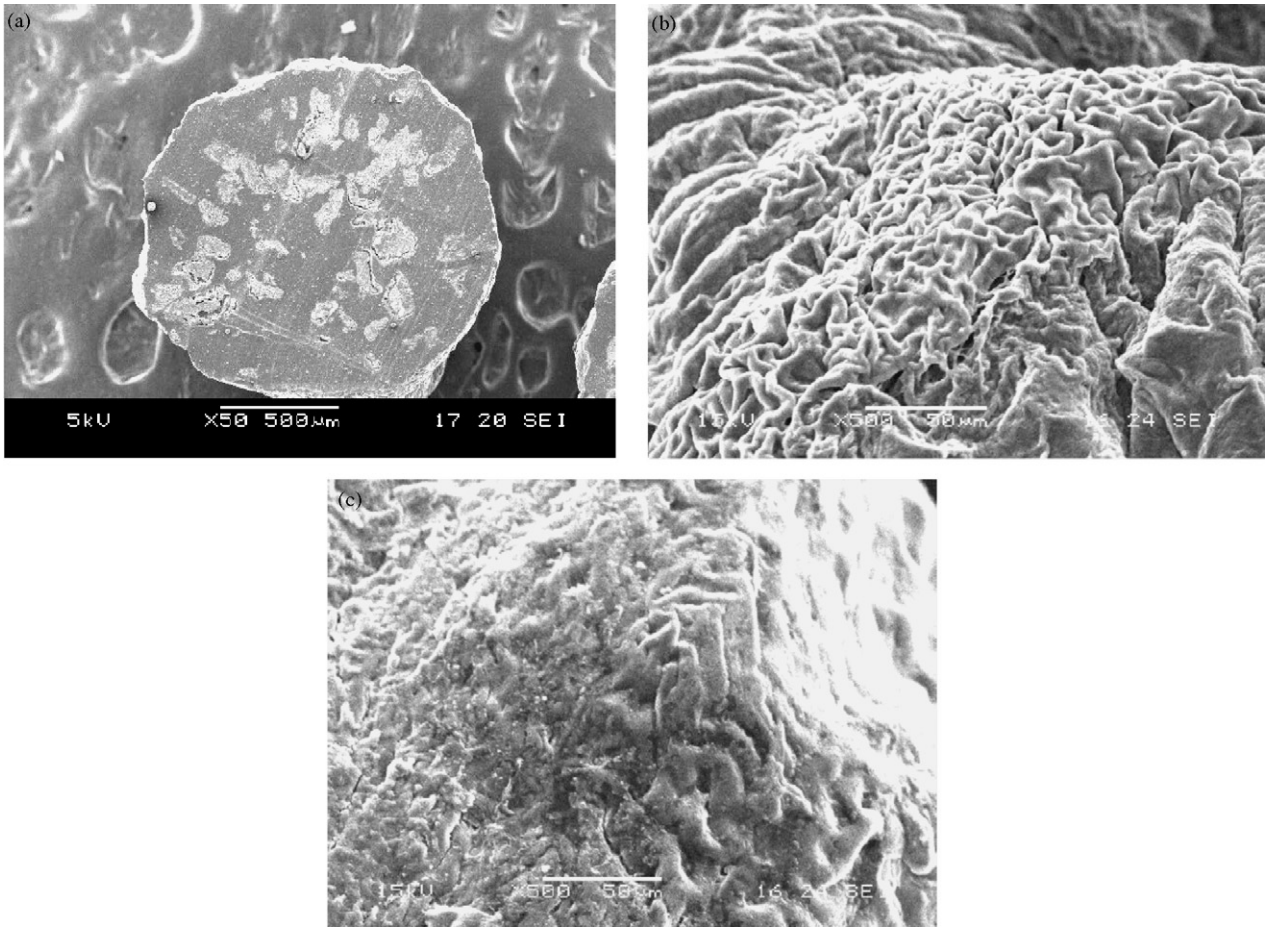


Fig. 1. SEM photograph of *Sargassum* immobilized PVA beads (30 g/L): (a) cross-sectional image, (b) surface image before copper uptake, (c) surface image after copper uptake.

Table 2
Size and weight of the PVA-seaweed beads before and after stirring

| | Blank beads | | PVA-*Sargassum* beads (30 g/L) | |
|---|---|---|---|---|
| | Before stirring | After stirring | Before stirring | After stirring |
| Mean diameter (mm) | 1.27 | 1.24 | 1.27 | 1.25 |
| Total dry weight (g) | 2.02 | 2.01 | 2.11 | 2.01 |

A stirring test was conducted on 2 g sample of both the blank and biomass-loaded PVA cryogel beads. The diameters and weights recorded in Table 2 show that the blank beads were robust and did not abrade significantly after stirring for 72 h. The 30 g/L PVA-*Sargassum* beads, however, showed a small weight loss (about 5%). The robustness of the beads is related to the properties of the support material and biomass as well as the shear stresses present due to hydrodynamic interactions, such as liquid shear, wall shear or collision between beads [14].

For the PVA-seaweed beads to perform satisfactorily during operation, it is necessary for the support material to be stable and robust over the wide range of pH expected under actual process conditions. Fig. 2 revealed that the blank PVA cryogel beads were very stable and remained intact over the pH range of 1–13. The weight loss of 30 g/L PVA-*Sargassum* beads remained at about 5% over the whole pH range. The immobilized *Sargassum* may have contributed to the weight loss. Khoo and Ting [9] had earlier reported that blank PVA cryogel beads showed negligible weight change in solutions of urea, EDTA, citrate and phosphate at various ionic concentrations.

### 3.3. pH profile for biosorption by PVA-Sargassum beads

Fig. 3 shows the biosorption of copper ions by freely suspended *Sargassum* and PVA-*Sargassum* beads as a function of pH (preliminary tests confirmed that the blank PVA cryogel beads exhibited only negligible copper uptake (data not shown), and corroborated our previous work on gold biosorption in a similar system [9]). Higher pH led to higher metal uptake. The uptake capacities of the two sorbents generally showed a similar

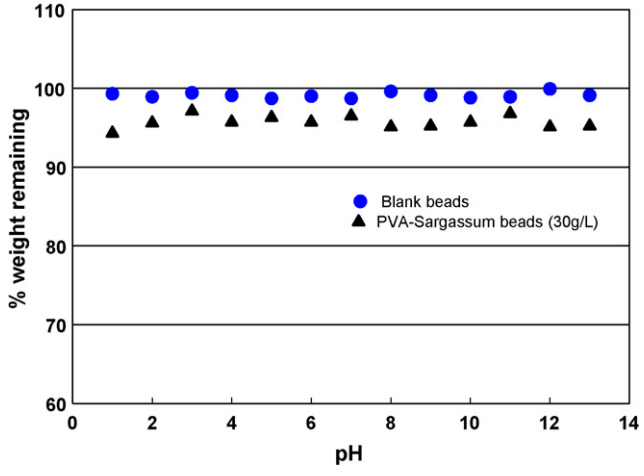


Fig. 2. Robustness of PVA beads as a function of solution pH.

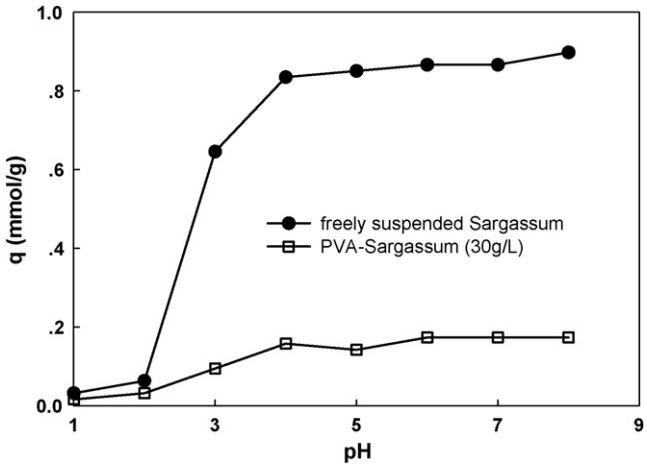


Fig. 3. Effect of pH on copper uptake by freely suspended *Sargassum* and PVA-*Sargassum* beads ($m$ = 1.0 g/L, $C_0$ = 1.5 mmol/L).

trend; an increase in uptake with pH increase at the lower pH range (pH 1.0–4.0), with the effect leveling off beyond pH 4.0. It was also noted that the PVA-*Sargassum* beads had a much lower uptake capacity than the freely suspended *Sargassum* at the same pH. The effect of pH on the uptake of metal ions by sorbents has often been reported; Iqbal and Edyvean [15] also noted the strong effect of pH on metal uptake by an immobilized biomass and attributed the pH dependence to the competition between the proton and metal cations for binding on the sorbent. The important role of proton was also reflected when Cu-laden *Sargassum* was washed with HCl; the increase in the final pH indicated that protons competed with the copper ions for the binding sites [16]. Indeed, the typical dependence of metal uptake on pH may also be attributed to the weakly acidic carboxyl groups (R–COOH) present in the algal cell wall. As the pKa of R–COOH is in the range 3.5–5.5 [1], more carboxyl groups will be deprotonated at pH over this range, and thus give rise to more negative binding sites. As a result, the metal uptake capacity the biomass is enhanced.

### 3.4. Biosorption isotherms of PVA-Sargassum beads

The results of the copper sorption isotherms are shown in Fig. 4. In all cases favorable isotherms are observed, and the data could be well modeled according to the Langmuir adsorption isotherm.

$$q = \frac{q_{\max} b C_e}{1 + b C_e} \tag{2}$$

where $C_e$ is the equilibrium metal concentration, $q_{\max}$ (based on the weight of the PVA-*Sargassum* beads) and $b$ is the Langmuir constants.

The results of Langmuir isotherms are presented as solid lines in Fig. 4 and summarized in Table 3. The sorption capacity of different sorbents could be compared by examining the Langmuir constant $q_{\max}$. Table 3 shows that all PVA-*Sargassum* beads had lower copper uptake capacity than the freely suspended *Sargassum*. Furthermore, a positive correlation was observed between copper uptake capacity and biomass loading concentra-

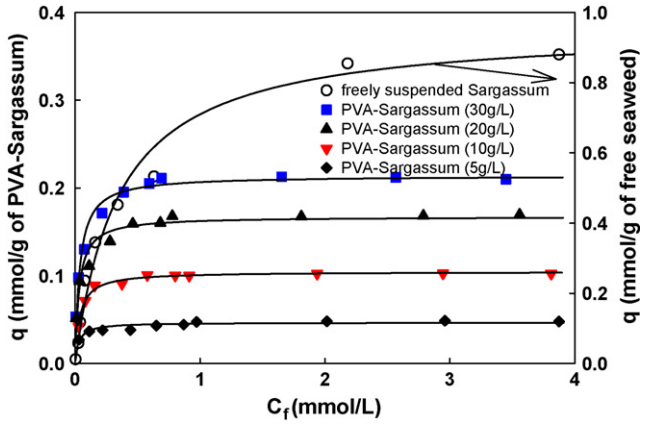


Fig. 4. Copper sorption isotherms of freely suspended *Sargassum* and PVA-*Sargassum* beads ($m$ = 1.0 g/L, pH 5.0).

tion within the beads. It is reasoned that more biomass embedded within the beads resulted in more binding sites, thus leading to a higher metal uptake capacity. The values of $q_{max}$ were also recalculated based on the weight of the biomass in the PVA-*Sargassum* beads and are shown in parenthesis in Table 3. It can be seen that the range of $q_{max}$ for all sorbents were within 10%, thus implying that the biomass within the PVA-*Sargassum* beads was mainly responsible for the metal binding. More importantly, the results also indicated that the biosorbent particles entrapped and retained within the bead were accessible to the metal ions. This was possibly due to the high water permeability of PVA cryogel beads which facilitated the diffusion of metal ions to the entrapped biomass, since the beads swelled rapidly when in contact with the aqueous solution.

The affinity constant, $b$, indicates the sorbent affinity at low metal concentrations, and hence a high value of the affinity constant is desirable for a better sorbent. Table 3 shows that PVA-*Sargassum* beads had a higher affinity than the feely suspended *Sargassum* for copper uptake, and the values of $b$ were not significantly affected by the concentration of the biomass within the beads. It may be reasoned that the immobilization matrix helps to stabilize the metal ions on the binding sites of the biomass, thus resulting in a higher affinity constant.

Bai and Abraham [17] have noted that increasing biomass loading within the bead led to an increase in metal uptake capacity, possibly due to an increase in the number of binding sites within the beads. Beyond a certain biomass loading concentration, however, a decrease in uptake occurred. A 'screening effect' may arise as the concentration of the biomass becomes denser at the outer layer of the beads [18], or an increase of biomass concentration may lead to interference between binding sites which leads to cellular aggregation [19], rendering some binding sites partially hindered to metal ions and thus a lower specific metal uptake capacity. Table 3 shows no evidence of significant interference or screening effect, even at 30 mg/L.

The sorption capacity of different sorbents also could be compared by examining the efficiency factor, i.e., the ratio of adsorption by the beads to sorption by free biomass. The values for the PVA-*Sargassum* beads in this work were calculated to be 0.22 (30 g/L), 0.18 (20 g/L), 0.10 (10 g/L) and 0.05 (5 g/L), respectively. An efficiency factor of about 0.83 had been reported for a 60 g/L PVA-fungus beads, which were fabricated with three cycles of freezing (<2 °C) and thawing (30 ± 2 °C) [17].

The adsorption data was also modeled using the Freundlich sorption isotherm:

$$q = kC_e^n \tag{3}$$

where $k$ gives a measure of the adsorbent capacity, and $n$ gives the intensity of adsorption. The modeling results are also incorporated in Table 3 where it could be seen that the Freundlich model was not as good as the Langmuir model in fitting the experimental data in the present case.

### 3.5. Kinetics studies of PVA-Sargassum beads

The effect of biomass loading, initial copper concentration and hydration on the kinetics of PVA-*Sargassum* beads are shown in Figs. 5–7, respectively. Two commonly used kinetic expressions, namely pseudo first-order and pseudo second-order equations were used to fit the experimental results.

The pseudo first-order rate expression of Lagergren is generally described as [20]:

$$q = q_e(1 - \exp(-k_1 t)) \tag{4}$$

The pseudo second-order expression is given by [21] as:

$$\frac{1}{q_e - q} - \frac{1}{q_e} = k_2 t \tag{5}$$

where $q_e$ and $q$ are the uptake capacity (mg/g) of the sorbent at equilibrium, and at any time $t$, respectively; $k_1$ and $k_2$ are

Table 3
Parameters for Langmuir and Freundlich isotherms (pH 5.0)

| | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | $q_{max}$ [a] | $b$ [b] | $r^2$ | $K$ [c] | $n$ | $r^2$ |
| PVA-*Sargassum* (5 g/L) | 0.05 (0.98) | 34.89 | 0.84 | 0.04 | 0.10 | 0.89 |
| PVA-*Sargassum* (10 g/L) | 0.10 (1.10) | 26.96 | 0.98 | 0.09 | 0.11 | 0.72 |
| PVA-*Sargassum* (20 g/L) | 0.17 (1.02) | 32.07 | 0.94 | 0.15 | 0.13 | 0.83 |
| PVA-*Sargassum* (30 g/L) | 0.21 (0.91) | 28.07 | 0.96 | 0.19 | 0.14 | 0.83 |
| Freely suspended *Sargassum* | 0.96 | 2.86 | 0.98 | 0.56 | 0.31 | 0.95 |

[a] mmol/g. The data in parenthesis are calculated based on the weight of the biomass in the PVA-*Sargassum* beads.
[b] L/mmol.
[c] (mmol/g)/(mmol/L)$^n$.

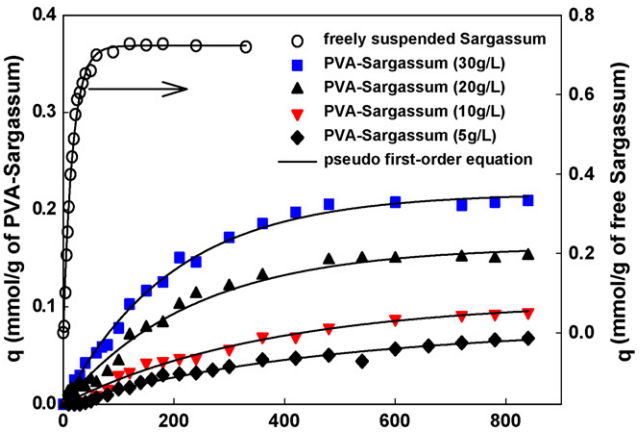


Fig. 5. Effect of concentration of the biomass loading on the uptake kinetics of PVA-*Sargassum* beads ($m$ = 1.0 g/L, $C_0$ = 1.5 mmol/L, pH 5.0).

the rate constants of the pseudo first- and second-order models, respectively. A non-linear regression analysis has been used to fit the experimental data using Eqs. (4) and (5), and the modeling results for $q_e$, $k_1$ and $k_2$ are presented in Tables 4–6 under various experimental conditions.

The effect of biomass loading concentration on the dynamics of the sorption process is shown in Fig. 5. A 90% of the total metal ions sorbed were achieved within 60 min by the freely suspended *Sargassum*. In contrast, PVA-*Sargassum* beads required at least 6, 6.5, 9 and 10.5 h at a biomass loading of 30, 20, 10 and 5 g/L, respectively to achieve 90% of total metal ions sorbed. The results revealed the mass transfer resistance exerted by the immobilization matrix during the metal uptake process. The resistance is related to factors such as the nature of the immobilization matrix, pore size of the sorbent, and the concentration of the loaded biomass. For example, higher biomass loading provides more metal binding sites, thus leading to a faster metal sorption rate as well as higher initial sorption rate (as manifested by initial slopes in Fig. 5). Intraparticle diffusion had been proposed as the rate-controlling step for the metal uptake of PVA cryogel beads [9].

Comparatively slower metal uptake rate had been reported for the biosorption of gold by immobilized fungal biomass [9]. Freely-suspended biomass required about 20 h to achieve 80% removal of the initial metal concentration whilst PVA-immobilized biomass required 33.5 h. In comparison, the alginate-immobilized biomass showed the greatest mass transfer resistance, requiring 265 h to achieve the same percentage of removal. de Rome and Gadd [6] reported an increase in the initial rate of sorption and uranium (in the form of $UO_2^{2+}$) removal rate when the biomass concentration (*Saccharomyces cerevisiae*) was increased from 30 to 70% of the immobilized alginate beads. Methods have been applied to improve the metal uptake kinetics. For example, it had been reported that the presence of alginate in the PVA cryogel beads accelerated the hardening of the beads

Table 4
Effect of concentration of biomass loading on the modeling of uptake kinetics by immobilized biomass ($m$ = 1.0 g/L, $C_0$ = 1.5 mmol/L, pH 5.0)

| PVA-*Sargassum* | Pseudo first-order equation | | | Pseudo second-order equation | | |
|---|---|---|---|---|---|---|
| | $q_e$ (×100) | $k_1$ (×100) | $r^2$ | $q_e$ (×100) | $k_2$ (×100) | $r^2$ |
| 5 g/L | 5.95 | 0.21 | 0.98 | 12.13 | 1.21 | 0.98 |
| 10 g/L | 10.65 | 0.27 | 0.98 | 15.46 | 1.31 | 0.98 |
| 20 g/L | 16.22 | 0.43 | 0.99 | 21.80 | 1.64 | 0.98 |
| 30 g/L | 21.68 | 0.50 | 0.99 | – | – | – |
| Freely suspended *Sargassum* | 92.33 | 5.83 | 0.99 | – | – | – |

*Note*: $q_e$ (mmol/g); $k_1$ (mm$^{-1}$); $k_2$ (g/mmol min).

Table 5
Effect of initial copper concentration on the modeling of uptake kinetics by PVA-*Sargassum* beads (20 g/L) ($m$ = 1.0 g/L, $C_0$ = 1.5 mmol/L, pH 5.0)

| Copper concentration (mM) | Pseudo first-order equation | | | Pseudo second-order equation | | |
|---|---|---|---|---|---|---|
| | $q_e$ (×100) | $k_1$ (×100) | $r^2$ | $q_e$ (×100) | $k_2$ (×100) | $r^2$ |
| 0.5 | 15.47 | 0.17 | 0.98 | 25.26 | 0.41 | 0.97 |
| 1.0 | 17.11 | 0.41 | 0.99 | 22.60 | 1.60 | 0.98 |
| 2.0 | 16.23 | 0.42 | 0.99 | 21.84 | 1.63 | 0.98 |

*Note*: $q_e$ (mmol/g); $k_1$ (mm$^{-1}$); $k_2$ (g/mmol min).

Table 6
Effect of hydration on the modeling of uptake kinetics by PVA-*Sargassum* beads (20 g/L) ($m$ = 1.0 g/L, $C_0$ = 1.5 mmol/L, pH 5.0)

| PVA-*Sargassum* beads | Pseudo first-order equation | | | Pseudo second-order equation | | |
|---|---|---|---|---|---|---|
| | $q_e$ (×100) | $k_1$ (×100) | $r^2$ | $q_e$ (×100) | $k_2$ (×100) | $r^2$ |
| Hydrated | 14.52 | 3.03 | 0.92 | 15.49 | 32.78 | 0.96 |
| Dry | 16.22 | 0.43 | 0.99 | 21.80 | 1.64 | 0.98 |

*Note*: $q_e$ (mmol/g); $k_1$ (mm$^{-1}$); $k_2$ (g/mmol min).

and markedly increased its porosity, hence improved the mass transfer rate of metal ions [22].

Results in Table 4 show that pseudo first-order equation fits well the kinetic results for the entire range of biomass loading concentration, with the correlation coefficients >0.98. The regressed $q_e$ were comparable with the results obtained from the Langmuir isotherm (Table 3); and the values of $k_1$ increased with an increase of biomass loading concentration. In contrast, the pseudo second-order equation fits well the data for 20, 10 and 5 g/L PVA-*Sargassum* beads, with correlation coefficients 0.98. Conformity of the kinetic data to the Lagergren first-order model had been reported for the Cr(VI) uptake by polyacrylamide-grafted sawdust, which was considered as a diffusion controlling process [23]. Others have reported biosorption systems which were well modeled by the pseudo second-order equation [24,25].

The effect of the initial copper concentration on the kinetic profiles of PVA-*Sargassum* beads (20 g/L) is shown in Fig. 6. An increase in the copper concentration from 0.5 to 1.0 mM gave rise to an increase in the initial rate of biosorption (initial slopes). A similar phenomenon has been reported earlier [9]. Higher metal concentration creates greater driving force for biosorption, especially when the mechanism for metal uptake in *Sargassum* is primarily reversible surface ion-exchange [4]. However, further increase in the copper concentration (from 1.0 to 2.0 mM) did not lead to a further increase in the uptake rate. This suggested that the surface binding sites on the immobilized biomass was saturated with surrounding metal ions, and had attained a maximum uptake rate. Costa and Leite [26] reported that an increase in the initial cadmium concentration from 20 to 41 mg/dm$^{-3}$ resulted in an increased initial rate of sorption by *Chlorella homosphaera* immobilized in alginate. Although they also observed that an increase in zinc concentration from 75 to 720 mg/dm$^{-3}$ led to a decrease in the initial rate, no explanation was offered for this anomalous phenomenon. The experimental data in Fig. 6 were well fitted by both models, with the results presented in Table 5. The values of $k_1$ and $k_2$ increased significantly when the initial copper concentration was increased from 0.5 to 1.0 mM, but remained relatively constant at 2.0 mM.

In order to investigate the effect of hydration of the beads on the kinetics of metal uptake, the 20 g/L PVA-*Sargassum* beads

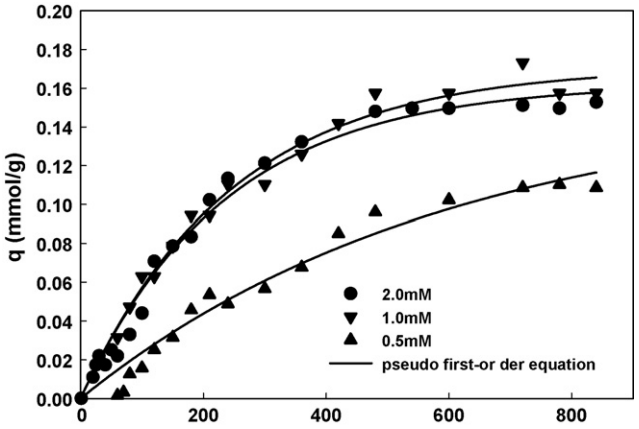


Fig. 6. Effect of initial copper concentration on the uptake kinetics of PVA-*Sargassum* beads (20 g/L) ($m$ = 1.0 g/L, $C_0$ = 1.5 mmol/L, pH 5.0).

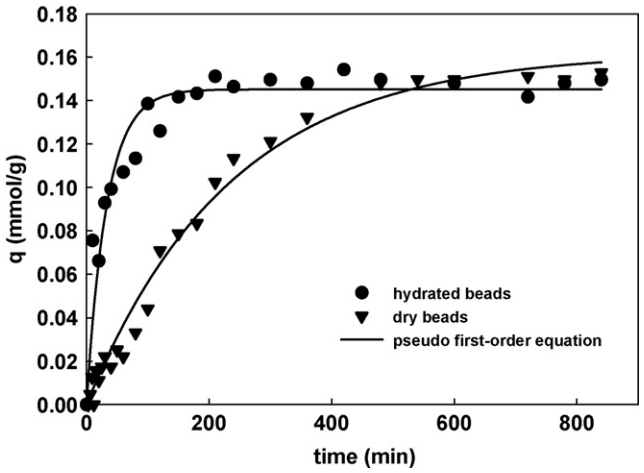


Fig. 7. Effect of hydration on the uptake kinetics of PVA-*Sargassum* beads (20 g/L) ($m$ = 1.0 g/L, $C_0$ = 1.5 mmol/L, pH 5.0).

were first soaked in ultra-pure water for 6 h before use. The kinetic results were compared with those of corresponding dry beads in Fig. 7. It is clear that soaking greatly improved the copper uptake rate; this may be due to the structural changes during the hydration process. The voids, pores and channels within the beads were hydrated when the beads became swollen in ultra-pure water, thus facilitating the diffusion of metal ions onto the active sites on the biomass surface. The results in Table 6 showed that the experimental results could be modeled by both the pseudo first and second-order equations, with the values of $k_1$ and $k_2$ for swollen beads being seven and 20 times that of the dry beads, respectively.

## 4. Conclusions

The characteristics of PVA cryogel as immobilization matrices were examined through a series of batch experiments. PVA cryogel beads were robust and stable under a wider range of pH (1–13). It is also shown that both surface area and pore size were greatly affected by the biomass loading content within the beads.

The PVA-*Sargassum* beads showed lower copper uptake capacity than the freely suspended *Sargassum*. A positive correlation was found between copper uptake capacity and biomass loading concentration (5–30 g/L) within the beads. It was also found that the uptake capacities of the beads were significantly affected by solution pH, with higher pH favoring higher metal-ion removal. Kinetic experiments demonstrated that the immobilization matrix exerted mass transfer resistance during metal uptake process. Metal uptake rates increased with a greater concentration of biomass embedded within the beads. For example, PVA-*Sargassum* beads required about 6, 6.5, 9 and 10.5 h at a biomass loading of 30, 20, 10 and 5 g/L, respectively to achieve 90% of the total metal uptake. A higher metal biosorption rate could also be obtained with an increase in initial copper concentration or by the hydration of beads before use. It is also shown that the experimental data were better modeled by the pseudo first-order equation than the pseudo second-order equation.

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