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New method for evaluation of heavy metal binding to alginate beads using pH and conductivity data

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Abstract Extensive research has been conducted for removal and recovery of heavy metals from wastewater and industrial wastewater in recent years. Due to its low cost and high sorption efficiency, alginate was extensively investigated as a biosorbent. It is known that the sorption of metals to alginate is rate limited. However, the sampling in the beginning of experiments, from 30 seconds to few minutes, is very difficult, if not impossible. In this study, a nontraditional experimental method was used to determine the removal kinetics of metals for short time periods. A relationship among pH, conductivity, and metal concentration was established. It was shown that the sorption mechanism was ion exchange for all metals investigated in this study. A series of experiments was conducted to determine the ion exchange kinetics of different metals at varying pH conditions. Second order pseudo rate kinetics was shown to define the experimental findings well. Results also showed that the extent of exchange significantly reduced as the pH decreased. The selectivity of metal exchange to alginate beads was determined. It was observed that the extent of the ion exchange was greatest for Cu^{2+} and lowest for Mn^{2+} and Fe^{2+}, following the order of $Cu^{2+} > Zn^{2+} \cong Co^{2+} \cong Ni^{2+} > Mn^{2+} \cong Fe^{2+}$.

Keywords Second order pseudo rate · Ion exchange · Kinetics · Alginate · Metal sorption · Biosorption

1 Introduction

Extensive research has been conducted for removal and recovery of heavy metals from wastewater and industrial wastewater in recent years. Precipitation (Navarro et al., 2005; Charerntanyarak, 1999; Bhagat and Burgess, 2004), electrokinetic methods (Mohammadi et al., 2004; Marder et al., 2004; Grimm et al., 1998), and ion exchange (Papadopoulos et al., 2004; Aklil et al., 2004; Volesky and Holan, 1995; Volesky, 2001) are few of the techniques that have been investigated in detail. Each method has its own advantage as well as disadvantage in terms of efficiency and cost. Precipitation yields high levels of removal; however, it is inefficient for the removal of metals at low concentrations. Electrokinetic methods may be very effective at removal of low concentrations of heavy metals, but they are not cost effective. Adsorption and ion exchange have shown to yield promising results in terms of high removal efficiencies and low cost. The sorption of metals to dead biological materials or to the materials that have been derived from living organisms has been widely investigated due to their cost efficiency, as well as their high removal capacity of heavy metals (Volesky and Holan, 1995; Volesky, 2001).

Biosorption is a process in which metal uptake occurs by microbial cells through adsorption, ion

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exchange, co-ordination and/or complexation (Volesky, 2001; Veglio and Beolchini, 1997). Alginate has become one of the important groups of adsorbent among the biological materials (Davis et al., 2003). Alginate, which is mainly obtained from brown algae, is a biopolymer composed of varying compositions of β-1, 4 D-mannurinic (M) and α-1, 4 L-guluronic (G) acids. Alginate has great affinity to divalent cations and its viscous solution forms gelation when it contacts with a divalent cation. Various results were reported for the binding mechanism of metals to alginates. There are some studies at which mainly ion exchange was observed (Schiewer and Volesky, 1995; Davis et al., 2003), and other studies reported sorption through complexation in addition to ion exchange (Davis et al., 2003). The ion exchange process involves exchanges between metal ions and other cations bound to various functional groups (carboxyl or hydroxyl) at the surface in aqueous solution. However, the sorption involves physical and chemical binding to a free surface. The extent of heavy metal sorption to alginate beads was studied comparatively for heavy metals in several studies. The level of the metal sorption to alginic acid extracted from *Laminaria digitata* was found to be in the order of $Cu^{2+} > Ba^{2+} > Ca^{2+} > Co^{2+}$ (Haug, 1961). In another study, it was found that the sorption of Cu^{2+} on alginate was much greater than the sorption of Zn^{2+} (Jang et al., 1999). Higher extent of sorption of copper was also observed with formaldehyde cross linked *Ascophyllum nodosum* seaweed biomass (de Calvalho et al., 1995). The degree of the sorption was observed in the order of $Cu^{2+} > Cd^{2+} > Zn^{2+}$.

Almost all comparative studies were conducted at equilibrium conditions. The kinetic experiments of metal sorption/ion exchange were focused on determining the type of ion exchange model. In a study, kinetics of copper ion uptake by calcium alginate was described using two-pK Basic Stern model (Chen et al., 1997). In a different study, copper uptake by alginate was represented using a pseudo second order kinetics (Beolchini et al., 2003). It was reported that the equilibrium was reached within 20 minutes. Although the equilibrium is reached in a short time (e.g. 20 minutes) sampling at shorter periods (e.g. 30 seconds) using traditional batch experiments has been a problem. Kinetics at early stages may be important for designing flow through systems and developing metal selective materials and filters for analytical purposes. Despite extensive research conducted in biosorption, the ion exchange kinetics of divalent metals in the early stages of the experiments is yet to be investigated. The main objectives of this study were to develop an experimental method to investigate the removal kinetics of metals starting from very early stages (e.g. 30 seconds) to the equilibrium, and to compare the rates and extents of removals of different divalent metals. To achieve this, a relationship among pH, conductivity and metal concentration was established. Then, the metal concentration was determined by measuring pH and conductivity. This allowed online data collection, which was later translated into exchanged metal concentration. Then a series of experiment was conducted to determine the ion exchange kinetics of various metals at three different initial pH conditions. Finally, sorption affinities of different divalent metal ions to alginate beads were compared.

2 Materials and methods

Low density sodium alginate was obtained from Sigma Chemical Co. (St. Louis, MO) and used as received. 2% of sodium alginate solution was prepared by adding 2 g of sodium alginate to 100 mL of distilled water. The solution was slightly heated (~50°C) and mixed with a magnetic stirrer at 500 rpm. The solution was left aside to rest for 24 hours to remove fine air bubbles generated during mixing. The prepared alginate solution was placed into a 50 mL of burette and drops were allowed to fall into a beaker filled with 0.5 N HCl solution. The beads were ellipsoid and approximately 2 to 3 mm in size with soft texture. Only 30 beads were generated for each experiment. Amount of alginate used to form 30 beads were recorded to determine the amount of alginate in the beads. The beads were taken out of the beaker and washed thoroughly with DI water until the conductivity of the washed water reduced below 11 μS/cm (the conductivity of DI water). Following the washing, the beads were taken onto a filtration paper to remove excess water.

Analytical grades of $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$, $MnSO_4 \cdot H_2O$, $FeCl_2 \cdot 4H_2O$ and $NiNO_3 \cdot 6H_2O$ were obtained from Merck and were used to prepare stock metal solutions. Metal analyses were conducted using a Flame Atomic Absorption Spectrometer (AAS) (Perkin Elmer 1100).

The experiments were conducted by placing 100 mL of predetermined concentration of metal solution into a beaker. A magnetic mixer was used to mix the solution at 500 rpm. The solution pH was adjusted to a predetermined value using only HCl solution. Following the pH adjustment, a conductivity probe was also placed into the beaker. Both pH and conductivity probes were fixed in the beaker using lab holders. The beaker was covered with a piece of parafilm to minimize the atmospheric interaction. Prepared alginate beads were added into the beaker and both pH and conductivity measurements were recorded at every 30 second using a multiparameter (WTW Multi340i). The calibration of pH and conductivity measurements of the instrument was made by using the standard pH (4.0, 7.0 and 11.0) and conductivity solutions obtained with WTW Multi340i. The calibration was checked using standard solutions before each experiment. All experiments were conducted at or below pH of 5.0. The reasons for this were two fold. First, it was assured that the predominant species of metals were divalent throughout the experiments. Second, the metals were entirely soluble in solution, and therefore no precipitation occurred. Zeta potential measurements were made using (Zeta-Meter 3.0+). First, alginate beads were air dried and then crashed into small particles using a glass mortar and pestle. Then, 100 mL of DI water was added to four different tubes and pH of each tube was adjusted to 2.0, 3.0, 4.0, and 5.0 using only dilute HCl solution. Crashed beads were added to each solution and then the zeta potential measurements were made at least five times at each pH value.

3 Results and discussion

3.1 Relationship among pH, conductivity, and metal concentrations

The conductivity is a measure of ion movement in solution and it is inversely proportional to resistivity. The conductivity of an aqueous solution depends on the concentrations of ions present in a solution, as well as their charge. Molar conductivity of a solution can be determined from its molar concentration and conductivity value measured using a conductivity meter as follows (Atkins, 1994).

$$\Lambda_m = \frac{\kappa}{C} \tag{1}$$

where, Λ_m is the molar conductivity (S cm^2/mol), κ is the conductivity (S/cm), and C is the molar concentration. The molar conductivity changes with the square root of the concentration based of Kohlrausch' Law (Atkins, 1994).

$$\Lambda_m = \Lambda_m^o - \chi\sqrt{C} \tag{2}$$

where, Λ_m^o is the limit molar conductivity at which ions do not interact with each other, and χ is a coefficient that depends on the stoichiometry. At low ion concentrations interaction among ions can be neglected and molar conductivity can be assumed to be equal to the limit conductivity values which are tabulated in reference books (Lide, 2003)

In an ion exchange process, metals in solution interact with other cations attached to the surface groups of the exchanger and as a result, exchange may occur. When alginic acid beads are used as ion exchanger, hydrogen ions diffuse into the solution as metals adsorbed on to the beads. Since the mobility of metal ions and hydrogen ions are different, the conductivity of the solution changes as follows:

$$\Delta\kappa = \Lambda^o_{m,H^+}\Delta C_{H^+} - \Lambda^o_{m,M^{+2}}\Delta C_{M^{+2}} \tag{3}$$

where, $\Delta\kappa$ represents the change in conductivity ($\Delta\kappa = \kappa_o - \kappa_t$), κ_o is the initial conductivity, κ_t is the conductivity at any time t, and the subscript M represents the metal. Hydrogen ions tend to increase the conductivity of the solution, whereas adsorbed metals reduce the conductivity due to their removed from the solution. An experimental result obtained for initial Cu^{2+} concentration of 300 mg/L and at a pH of 4.0 is presented in Fig. 1. The value of pH decreased and the conductivity increased with time, since the number of the hydrogen ions entering to the solution. The increase in conductivity is expected since the ionic mobility of H$^+$ is much greater than that of Cu^{2+}.

The concentrations of anions can be assumed to be constant throughout the soption process. Thus, it does not change the conductivity. If the process is assumed to be entirely ion exchange, two hydrogen ions are removed from the solid surface for every metal ion sorbed. Therefore, Eq. (3) can be written as a function of H$^+$ ion concentration as follows.

$$\begin{aligned}\Delta\kappa &= \Lambda^o_{m,H^+}\Delta C_{H^+} - \Lambda^o_{m,M^{+2}}\frac{\Delta C_{H^+}}{2}\\ &= \left(\Lambda^o_{m,H^+} - \frac{\Lambda^o_{m,M^{+2}}}{2}\right)\Delta C_{H^+}\end{aligned} \tag{4}$$

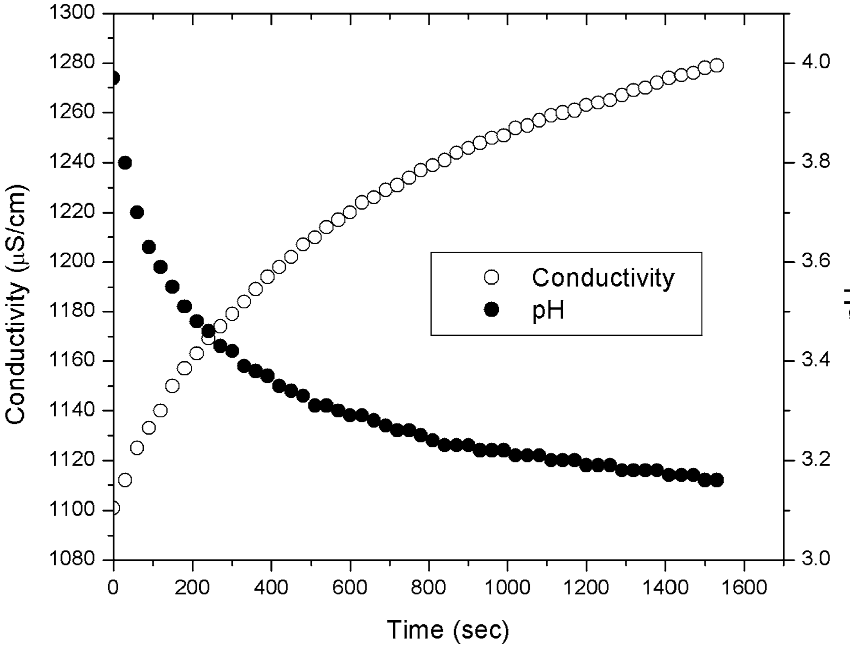


Fig. 1 Typical variation of pH and conductivity with time over the course of experiment (Initial pH = 4.0 and initial Cu^{2+} concentration = 300 mg/L)

Using the Eq. (4), the change of H^+ concentration (ΔC_{H^+}) can be determined if the change in conductivity ($\Delta\kappa$) is known. Both pH and conductivity measurements can be made while the experiment is conducted. If the ΔC_{H^+} values obtained from the pH measurements (pH_o-pH_t) is the same as the values obtained from conductivity data, then the assumption of pure ion exchange is said to be valid. The results for six different metals at concentrations of 300 mg/L and pH of 4.0 are presented in Fig. 2. The graph depicts the measured change in H^+ ions, which was obtained from pH measurements, as the x-axis versus predicted change in H^+ ions, which were obtained from conductivity measurements, as the y-axis (Eq. (4)). In all six cases, the slopes of linear fits were 1.00 ± 0.03, suggesting that the uptake mechanism of all six metals by alginate was purely ion exchange. Various results in the literature were presented with no common agreement about the uptake mechanism of metals by the alginate. In a study, Cd^{2+} sorption to Ca-Alginate beads was shown to be ion exchange dominant involving COO^- groups (Romero-Gonzalez et al., 2001). In a different study, it was shown that the sorption of Cu^{2+} and Al^{3+} was significantly reduced as a result of esterification of COO^- groups. However, the sorption of Au^{3+} was enhanced with esterifaction (Gardea-Torresday et al., 1990), suggesting strong ion exchange interaction for Cu^{2+} and Al^{3+}. Other researchers reported that Pb^{2+} exchange was pure ion exchange with Ca^{2+} bound to COO^- surface groups. Nevertheless, Cu^{2+} sorption was due to both ion exchange and surface complexation (Chen et al., 2002).

Since metal removal occurred only due to ion exchange, the concentration of metal associated with adsorption can be determined directly from pH measurements. For each metal ion, two hydrogen ions diffuse into the solution. The metal adsorbed concentrations will be half of the hydrogen ion concentration. This technique allows studying the metal sorption kinetics from very short time periods to the equilibrium. Taking samples and analyzing these samples in such short periods would otherwise be too difficult, if not impossible. However, it should be noted that the technique is valid in the presence of a single type of metal and hydrogen ions. In the presence of multiple metals, the concentration of a single metal can be determined if the concentrations of all the others are known. Although the method has limited application, it provides important information related to mechanism of the sorption of metals to alginate beads. In order to confirm the findings four different copper concentrations were equilibrated two hours with prescribed amount of alginate beads and the adsorbed Cu^{2+} mass predicted by the change of pH as well as by the analysis using AAS. Results

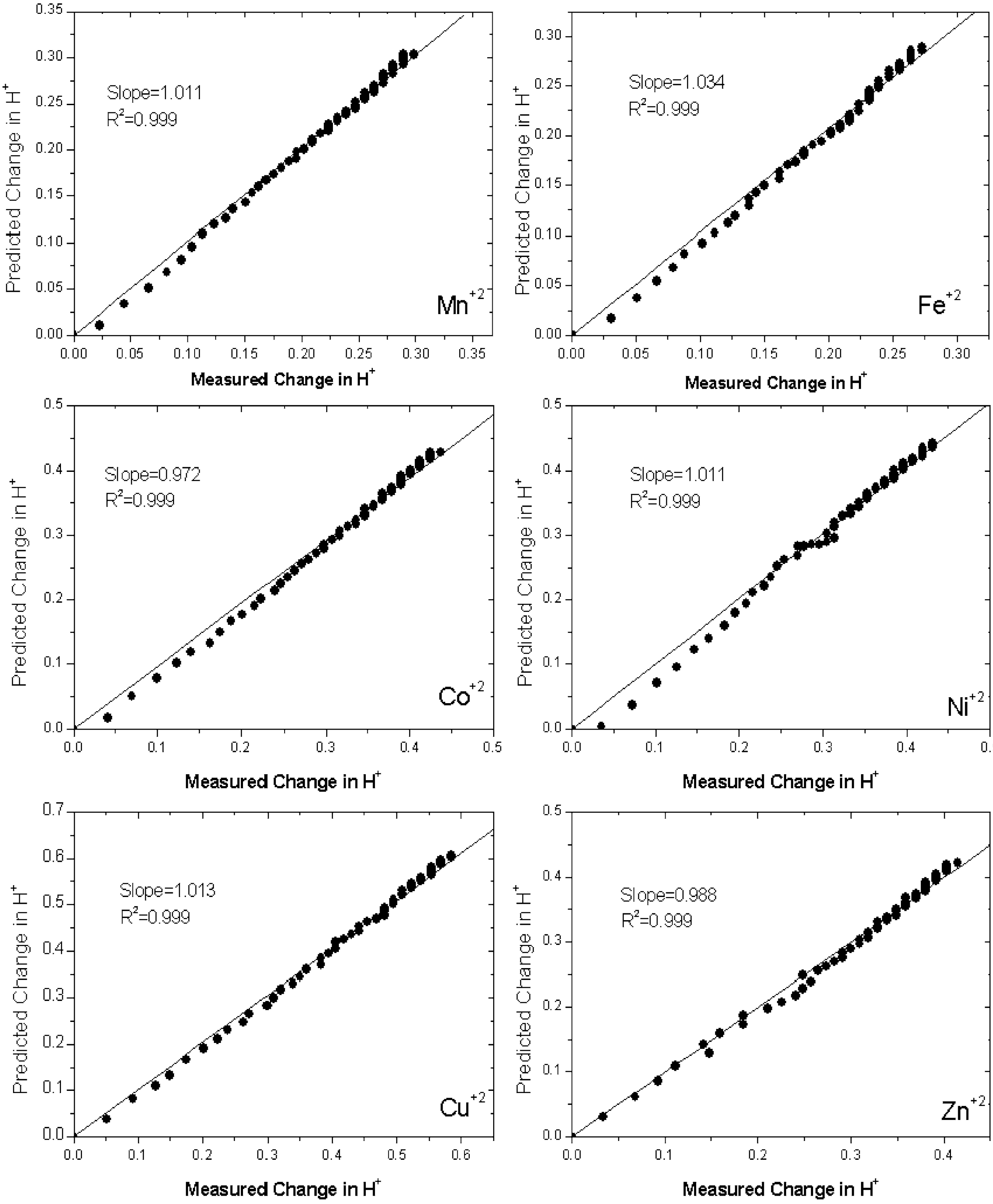


Fig. 2 Correlation between measured and predicted change in hydrogen ions (Initial pH = 4.0 and initial metal concentration = 300 mg/L)

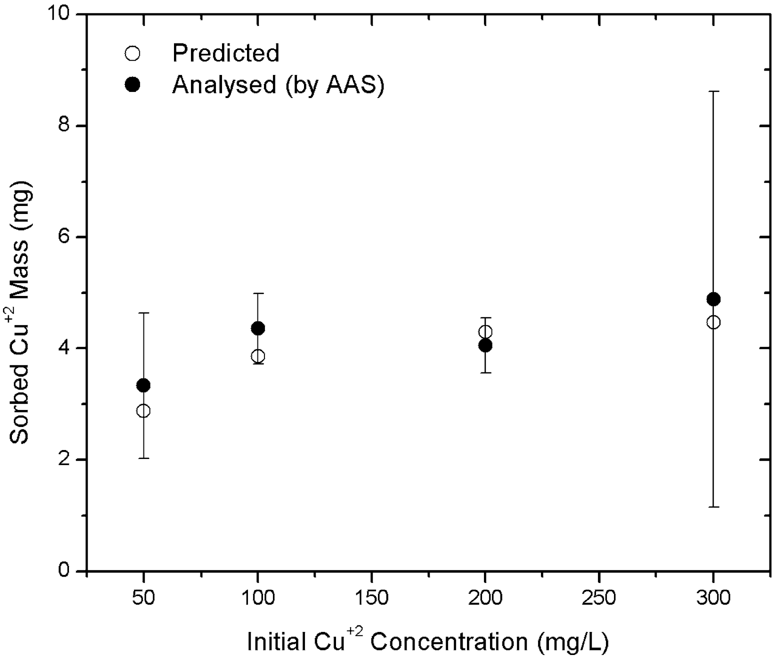


Fig. 3 Comparison between the predicted and analyzed exchanged Cu^{2+} mass by the pH and conductivity measurements, and atomic adsorption spectroscopy

obtained from AAS were within the range of the predicted value as can be seen from Fig. 3. The error bars represent the 95% confidence intervals of AAS analysis. The experiments with initial Cu^{2+} of 300 mg/L yielded much greater variations in AAS analysis, which was attributed to the errors in the dilution step.

3.2 Ion exchange kinetics

The experimental findings were successfully represented by a pseudo-second order kinetic model. A pseudo-second order kinetics has been extensively used to represent the kinetics of adsorption and ion exchange (Ho and McKay, 2000; Ho et al., 2003; Ozacar and Sengil, 2005). Alginate and metal reactions may be described as follow similar to the reaction developed for peat and copper (Ho and McKay, 1999).

$$2HA + \mathrm{Me}^{+2} \Leftrightarrow \mathrm{MeA}_2 + 2H^+ \tag{5}$$

where, HA is the alginic acid, and Me is the divalent metal. Based on this reaction, a relationship for the rate can be expressed as:

$$\frac{d(HA)_t}{dt} = k\,[(HA)_o - (HA)_t]^2 \tag{6}$$

where, $(HA)_o$ and $(HA)_t$ represents number of active sites on alginate at equilibrium and at time t, repectively. Assuming that the sorption capacity is proportional to the number of active sites occupied on sorbent, then the model can be represented as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{7}$$

where, k is the rate constant of ion exchange (g/mg/sec), q_e the amount of metal exchanged at equilibrium (mg/g), q_t the amount of metal exchanged at any time (mg/g), and t is the time (seconds). The solution and the linearized form of the kinetics can be represented as follows:

$$\frac{t}{q_t} = \frac{1}{q_e^2 k} + \frac{1}{q_e} t \tag{8}$$

The rate constant and exchanged mass at equilibrium can be found by plotting t/q_t against t. The linear fit the experimental data of Cu^{2+} at pH values of 3.0, 4.0 and 5.0 is presented in Fig. 4. Data obtained at pH of 3.0 was relatively scattered compared to those obtained at 4.0 and 5.0, which was a result of slow change of concentration with time. Accurate fits were obtained at those pH values for which the regression coefficients were greater than 0.99. The whole set of fitted kinetic

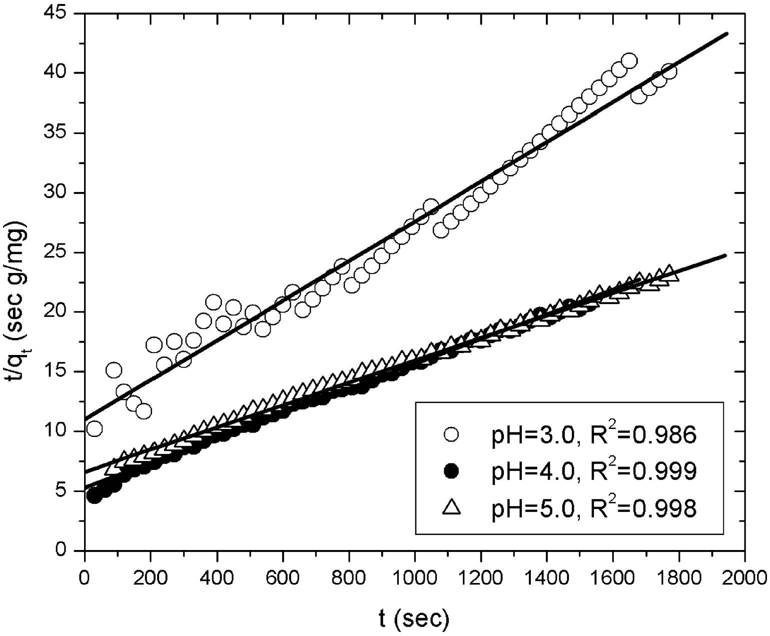


Fig. 4 Linearized pseudo second order model fit to the experimental data at various pH values at the initial Cu^{2+} concentration of 300 mg/L

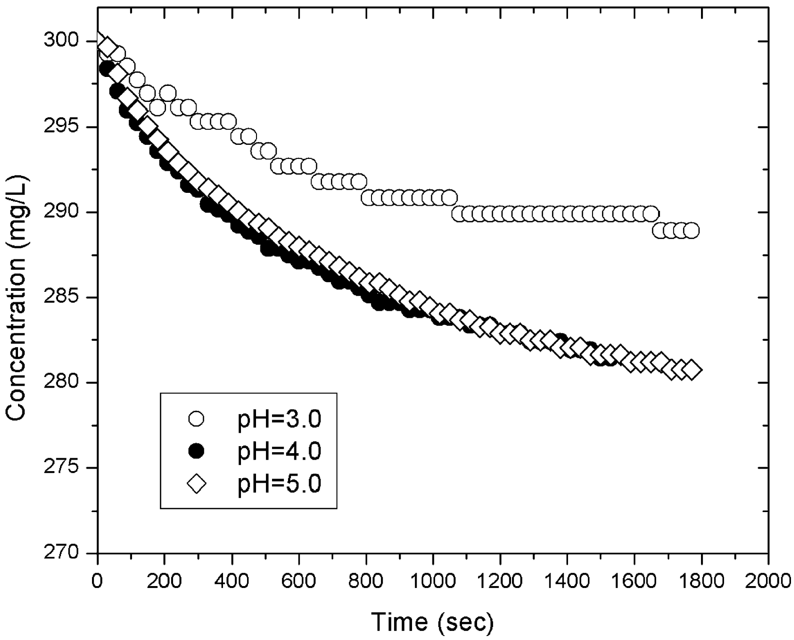


Fig. 5 Effect of pH on the change of concentration of Cu^{2+} with time

parameters as well as the exchanged equilibrium mass values predicted by the model are presented in Table 1. The effect of pH on the removal of copper from aqueous media is presented in Fig. 5 as an example. In most cases, the extent of sorption was slightly greater at pH of 5.0 than those observed at 4.0. However, the degree of the sorption was approximately less then 50% at pH of 3.0. This can be attributed to the fact that the protonation of alginic acid is more favorable at low pH conditions. Zeta potential measurements implied similar conclusions. The change of zeta potential of alginate particle with pH is presented in Fig. 6, where the error bars represent the standart deviations. While the zeta potential was about −80 mV at pH of 5.0, it increased to approximately −8 mV at pH of 3.0. No movement was observed at pH of 2.0. Therefore, the

Table 1 Summary of the rate coeficients and the exchanged mass values at equilibrium obtained from pseudo second order model fit (exchanged mass was represented as per g dry mass)

	pH = 3.0			pH = 4.0			pH = 5.0		
	q_e (mg/g)	q_e (mmol/g)	$k \times 10^5$ (g/mg/sec)	q_e (mg/g)	q_e (mmol/g)	$k \times 10^5$ (g/mg/sec)	q_e (mg/g)	q_e (mmol/g)	$k \times 10^5$ (g/mg/sec)
Cu	61.7	0.971	2.277	96.2	1.513	2.050	106.4	1.674	1.341
Fe	27.1	0.485	3.814	35.3	0.633	4.366	37.2	0.666	6.143
Mn	N/A	N/A	N/A	40.7	0.740	5.113	N/A	N/A	N/A
Zn	25.4	0.388	15.148	66.2	1.012	2.933	68.5	1.047	3.514
Co	39.5	0.671	4.796	62.9	1.067	3.557	70.4	1.195	2.793
Ni	39.1	0.666	3.551	62.5	1.065	3.596	68.0	1.159	3.373

N/A: Not available.

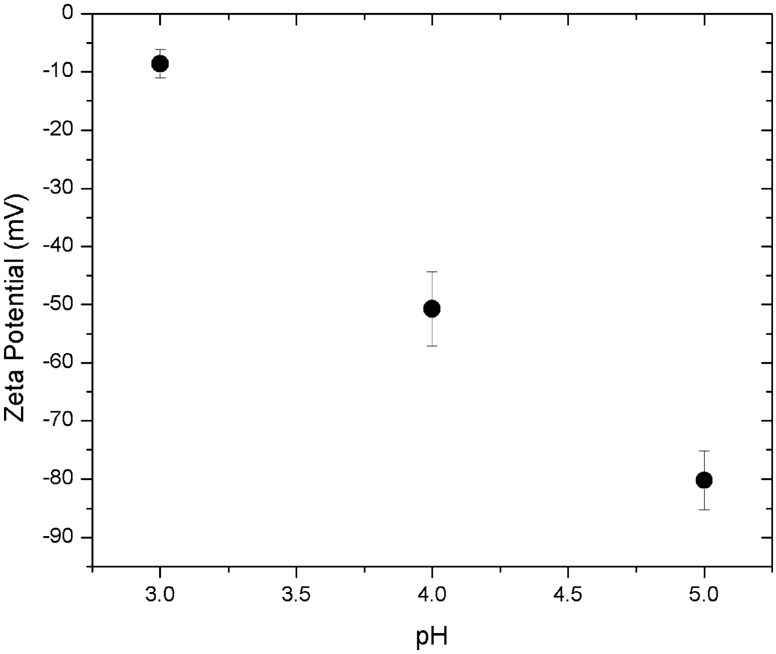
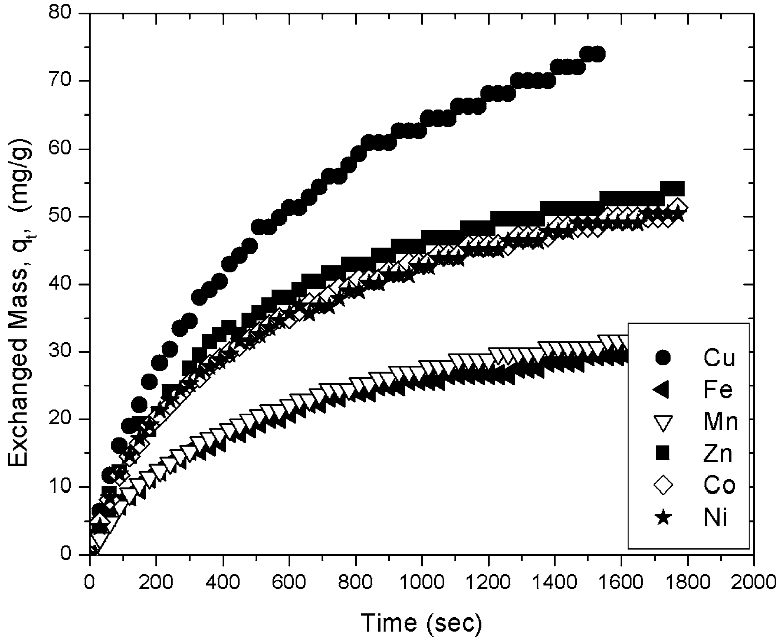


Fig. 6 Change of zeta potentials of alginate beads with pH

binding affinity of cations to alginate beads decreased as pH decreased.

The exchanged amounts of mass for six different metals at pH of 5.0 are presented in Fig. 7. The degree of sorbed Cu^{2+} was the greatest compare to the other five metals. Zn^{2+}, Co^{2+} and Ni^{2+} followed Cu^{2+} without any significant difference among each others. Although the difference was not apparent, Zn^{2+} showed a slightly higher exchange than Co^{2+} and Ni^{2}. Mn^{2+} and Fe^{2+} were the least sorbed compared to the other four metals. Since the molecular weights of these metals are very close to each other, the variation can not be due to the selection of unit (mg/L instead of mole/L). The exchanged mass amounts at equilibrium are presented both in mg/L and mmole/L in Table 1. In all pH values, the order of exchange was observed to be $Cu^{2+} > Zn^{2+} \cong Co^{2+} \cong Ni^{2+} > Mn^{2+} \cong Fe^{2+}$. These results are comparable to those reported in the literature for Cu^{2+} and Zn^{2+} binding to formaldehyde-cross-linked *Ascophyllum nodosum* seaweed biomass (de Calvalho et al., 1995). It was reported that the extent of sorption of various metals depended on the ratio of G and M contents of alginate (Davis et.al., 2003a, b). It is been known that the higher content of G blocks promoted the selectivity of divalent over monovalent cations. Among the

Fig. 7 Influence of the metal type on ion exchange of the alginate beads (Initial pH = 4.0 and initial concentrations = 300 mg/L)



divalent cations, the size of the metal may have an important effect on the selectivity of sorption. In a study, it was found that the selectivity of Cd and Ca increased compare to smaller Mg as G frequency increased in alginate extracted from *Sargassum* brown algae. In that study, Davis et al. (2003b) showed that the size had no apparent effect on the sorption since the most metals had similar ionic radii. Mn has the greatest ionic radii (0.83 Å, VI-fold coordination) and Ni has the smallest (0.69 Å, VI-fold coordination) among the metals used in this study. Shaw et al. (2003) showed that the retention of transition metals in a CS12A column followed the order of Pb(II) > Cu(II) > Cd(II) > Ni(II) > /Co(II)/Zn(II) > Mn(II) > Fe(II). CS12A was a phosphonate-carboxylate polymeric ion exchanger. The observed order of corresponded to the stability constants of metals complexes between these ions and ligands containing carboxylate functional groups. Interestingly, this order followed a similar trend to Irving-Williams series for the stability of metal complexes. Similar behavior was observed in this study. It can be concluded that the order of the exchange observed is a result of ability of exchange of individual metals with hydrogen ions associated with COO^- groups.

The rate coefficients were highly related to the extent of the soption. Lower rate coefficients were observed for those metals with higher equilibrium exchanged mass. This can be attributed to the size and crystal structure of hydrated metal ions. Diffusing into the pores of alginate beads may be a limiting step in this process. The change of rate coefficients with pH was various for different metals. While the rate coefficients decreased for Cu^{2+} and Co^{2+}, it increased for Fe^{2+} and remained unchaged for Ni^{2+} with increasing pH. However, the rate coefficient first decreased then increased for Zn^{2+}. The higher k values with pH observed for Fe^{2+} may be attributed to the fact that the extent of the exchange at various pH values was not as much as the other metals. Most likely Fe^{2+} interacted with mostly surface functional groups and therefore the exchange completed faster. For Cu^{2+} and Co^{2+} diffusion to the pores may be the rate limiting step. Since more sites are available for exchange at higher pH values, slower equilibrium was attained for Cu^{2+} and Co^{2+}. The odd behavior on Zn^{2+} was not clearly understood. High rate coefficient at pH of 3.0 may be an experimental error.

4 Conclusion

It was shown that the concentration of metals can be determined using pH and conductivity data measurements. The method was shown to be successful in determining the rates of sorption of metals to alginate beads including the early initial stages of the experiment. It must be noted that the technique is applicable only for pure ion exchange processes and relatively idealized solutions in the presence of a single type of metal ions. A further study may be needed to explore the sorption of metals at lower concentrations and at longer equilibration times. It was found that the sorption mechanism to alginate beads for all six metals was ion exchange. The pseudo second order model represented the experimental data extremely well The extent of the exchange was negatively affected as pH decreased. This was attributed to the lower surface charge of the surface at lower pH values, which was supported by zeta potential measurements. Smaller rate coefficients were found for those metals with higher sorbed mass at equilibrium. The extent of the exchange was the greatest for Cu^{2+} and the lowest for Mn^{2+} and Fe^{2+}, following $Cu^{2+} > Zn^{2+} \cong Co^{2+} \cong Ni^{2+} > Mn^{2+} \cong Fe^{2+}$ order.

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