

## REMOVAL OF COPPER AND CADMIUM IONS FROM AQUEOUS SOLUTIONS USING MODIFIED MARINE ALGAE (ALGINATE)

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### ABSTRACT

Adsorption techniques are widely used to remove pollutants from wastewater. In recent years, numerous approaches have been studied for the development of low-cost and effective adsorbents. Alginate obtained from seaweeds is cheap and abundant material. In order to improve its stability in aqueous medium, alginate-graft-poly(methyl methacrylate) was prepared by free radical copolymerization of methyl methacrylate onto the backbone of sodium alginate in aqueous medium. Batch adsorption experiments were carried out for the removal of copper and cadmium using alginate-graft-poly(methyl methacrylate) beads as an adsorbent. The graft copolymer prepared was characterized using FTIR, TGA, and SEM. Adsorption parameters such as initial pH, initial metal ion concentration and contact time were also studied. The results showed the stability of sodium alginate in aqueous media after the modification has been improved greatly. The Langmuir isotherm model fitted better than Freundlich model, suggesting monolayer adsorption prevailed in the adsorption process. The maximum adsorption capacity for the removal of the copper and Cadmium ions were 333 and 294 mg/g, respectively. The regeneration studies were carried out for multiple times. No significant loss of adsorption capacity was observed from the adsorbent. The adsorbent could be used in the treatment of waste water containing heavy metal ions (Cu and Cd).

**Keywords:** Alginate, radical, polymerization, remediation, wastewater

### 1 INTRODUCTION

The presence of toxic heavy metal ions in natural and industrial wastewater and their efficient removal is an important and widely studied research area. Metal ions such as lead (Pb), chromium (Cr), cadmium (Cd), copper (Cu), Arsenic (As), Iron (Fe), and Zinc (Zn) are commonly found in the environment. Many industries are responsible for the release of heavy metals into the environment through their wastewater (Fu and Wang, 2011). Conventional methods for treatment of polluted water laden with heavy metals include chemical precipitation (Minamisuwa *et al.*, 2004), advanced oxidation (Gunten, 2003), ion-exchange (Dizge *et al.*, 2009), adsorption (Huang *et al.*, 1996) and membrane filtration (Cemal, 2011, Kozlowski and Walkowiak, 2002). All these processes have their merits and limitations. Adsorption using low-cost material has been recognized as a potential alternative for the removal of toxic metal ions (Bailey *et al.*, 1999 and Abdel-Halim *et al.*, 2003). Many low-cost natural materials such as starch, cellulose, agricultural waste, and polysaccharides have been studied for their potential use as adsorbents for heavy metals (Kurniawan *et al.*, 2006). Alginic acid or its salts called alginates (Figure 1) is an important polysaccharide consisting the residues of  $\beta$ -1,4-linked-D-mannuronic acid (M-block) and  $\alpha$ -1,4-linked-L-guluronic acid (G-block) (Haug and Olav, 1966). It is a cheap and abundant polysaccharide mainly obtained from seaweed species. Alginate possesses metal sequestering properties and can effectively sequester dissolved metal ions in solutions quickly. Alginate readily dissolves in water to form viscous solution. In addition, it forms gels upon interaction with divalent metal ions particularly with  $\text{Ba}^{+2}$ ,  $\text{Sr}^{+2}$  and  $\text{Ca}^{+2}$ . In the Previous studies calcium alginate beads have been investigated for the removal of heavy metal ions from aqueous solution (Chen *et al.*, 1997 and Lai *et al.*, 2008). Removal of copper (II) ions from aqueous solutions using calcium alginate beads was reported by another research group. Their findings

revealed that removal percentages increased significantly for metal concentrations less than 0.1 mmol/L at pH 1.2 to 4, and plateau was established at pH > 4. The maximum metal removal capacities ( $q_{\max}$ ) were 130 mg/g and 416 mg/g for lead and copper, respectively (Chen and Wang, 2003). Papageorgiou *et al.*, 2007, reported the sorption of heavy metals by calcium alginate beads derived from *Laminaria digitata* in acidic solutions. They found that mannuronic acid residue was responsible for the ion exchange mechanism. The sorption capacity reached a maximum value at pH 4.5, sorption capacity with respect to  $\text{Cu}^{+2}$  was 87.39 mg/g and 129.95 mg/g was observed for  $\text{Cd}^{+2}$ . Magnetically modified alginic acid was prepared by means of entrapment method with iron oxide and urethane. The adsorbent had a maximum uptake capacity of 118 mg/g for  $\text{Cd}^{+2}$  at pH 4. It was established that adsorption of the metals was mainly performed by carboxyl groups of alginic acid (Jeon *et al.*, 2007).

To overcome the solubility of alginate in aqueous media as well as to improve its sorption capacity, grafting of vinyl monomers has been commonly used (Mishra *et al.*, 2010, Yadav *et al.*, 2011). Grafting can be carried out using redox initiators (Patel *et al.*, 1999), thermal initiators (Nuran and Murat, 2010), or using microwave irradiation (Nuran and Mustafa, 2013, Rani *et al.*, 2013). In the present study, poly(methyl methacrylate) was grafted on alginate using benzoyl peroxide initiator and the graft copolymer was evaluated for the removal of copper (II) and cadmium (II) from the aqueous solutions.

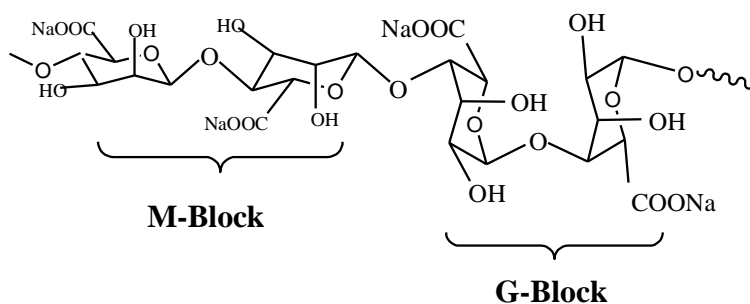


Figure1. Molecular structure of sodium alginate

## 2 EXPERIMENTAL.

### 2.1 Materials

Sodium alginate, methyl methacrylate (MMA), acetone, methanol and benzoyl peroxide (BPO) were purchased from Sigma-Aldrich (USA), MMA monomer was distilled under reduced pressure prior to use. BPO was further purified by dissolving in chloroform and precipitated in excess methanol. Stock solution of metals solutions concentration 1000 mg/L (copper and cadmium) were prepared by dissolving 3.790 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 2.103 g of cadmium nitrate separately in 250  $\text{cm}^3$  of deionized water respectively. The solutions were diluted to 1 litre in standard volumetric flasks. Different concentrations of the metal solutions were prepared by serial dilution of the stock solutions using deionized water. Other chemical reagents were of analytical grade and used as received.

#### 2.1.1 Graft copolymerization reaction

The grafting reactions were carried out under nitrogen atmosphere in a 250 mL three-necked flask equipped with a reflux condenser and a magnetic bar stirrer, immersed into oil bath. Nitrogen gas was purged into the flask to remove oxygen during the reaction. Known amount of sodium alginate was added into the reaction flask containing distilled water (100 mL). After sodium alginate was completely dissolved, the required amount of BPO dissolved acetone was added slowly to the reaction flask. The mixture was stirred for 20 min and the required amount of MMA was added. After the reaction time was over, the slurry was poured into methanol to induce precipitation. The precipitate was filtered, washed with acetone, dried in a vacuum oven at 60°C until a constant weight and kept in

a desiccator. The graft copolymer samples thus obtained were extracted for 24 h using acetone by Soxhlet extraction to remove the poly(methyl methacrylate) homopolymer. Finally the graft copolymer samples (Alg-g-PMMA) were dried at 60°C to constant weight. The grafting percentage G (%) and grafting yield were calculated using Equation (1) & (2), respectively, (Singh *et al.*, 2007).

$$G (\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

$$Y (\%) = \frac{W_2 - W_1}{W_3} \times 100 \quad (2)$$

where  $W_1$  is the initial weight of alginate,  $W_2$  is the weight of the graft copolymer after Soxhlet extraction and  $W_3$  is the weight of MMA.

### 2.1.2 Batch Adsorption and Kinetic Experiments

The standard stock solutions of metal ions (1000 mg/L) were diluted with deionized water to obtain desired concentrations. Adsorption studies were carried out using a 250-mL Erlenmeyer flask. The flasks were agitated on orbital shaker set at 200 rpm. A known amount of adsorbent was added in the sample solution whose concentration and pH were determined. After a specified time the solution was filtered and the remaining metal ions were analyzed using atomic absorption spectrometry. The amount of metal ions adsorbed by the adsorbent at equilibrium and the removal efficiency (%) were calculated using equation (3) and (4) respectively. Kinetics experiments were conducted using metal concentration of 200 mg/L for the two different metal ions. Adsorbent (0.1 g) were added to Erlenmeyer flask (250 mL) containing 50 mL of metal solutions and shakes at 200 rpm using Orbital shaker. Samples of 5 mL solution were withdrawn at pre-determined time interval using a syringe and analyzed for residual metal ions.

$$q_e (\text{mg/g}) = \frac{C_0 - C_e}{W (\text{g})} \times V (\text{L}) \quad (3)$$

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_F}{C_0} \times 100 \quad (4)$$

where  $C_0$  is the initial metal ions concentration (mg/L), and  $C_F$  is the metal ions concentration in the solution (mg/L) at the end of adsorption,  $C_e$  is the equilibrium concentration of metal ions in solution (mg/L),  $V$  is the volume of metal ions solution used (L) and  $w$  is the weight of the adsorbent used (g).

### 2.1.3 Characterization

The spectra of alginate and the graft copolymer (Alg-g-PMMA) were analyzed using Fourier transform infrared (FTIR) spectrometer (Perkin Elmer, USA). The samples were scanned in the wavelength range of 650-4000  $\text{cm}^{-1}$ . Thermogravimetric analyses (TGA) of alginate and Alg-g-PMMA were carried out using Q500TGA Thermal analyzer (USA). A temperature calibration test was conducted by running calcium oxalate monohydrate sample as standard. The analysis was conducted in an inert atmosphere from 30°C to 800°C at a heating rate of 20°C  $\text{min}^{-1}$ .

The scanning electron microscope (SEM) picture of sodium alginate, Alg-g-PMMA bead and its surface morphology were examined using JEOL JSM 6390LV (Japan). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold using auto fine coater (model JFC-1600).

### 3 RESULTS AND DISCUSSION

#### 3.1 Characterization

##### Infrared Spectroscopy

The FT-IR spectra of sodium alginate and Alg-g-PMMA are shown in Fig 2 (a) and (b) respectively. The broad peak at  $3426\text{ cm}^{-1}$  (Fig 2 (a)) is assigned to O-H stretching vibration. The peaks observed at  $1600$ ,  $1407$ , and  $1028\text{ cm}^{-1}$ , were due to stretching vibrations of  $\text{COO}^-$  (asymmetric),  $\text{COO}^-$  (symmetric), and C-O respectively. While additional new absorption peaks at  $2994$  and  $1730\text{ cm}^{-1}$  were assigned to stretching of C-H of methyl groups and ester carbonyl stretching, respectively. The presence of these peaks substantially confirmed the grafting of PMMA onto alginate in the spectrum of Alg-g-PMMA in Fig. 2 (b).

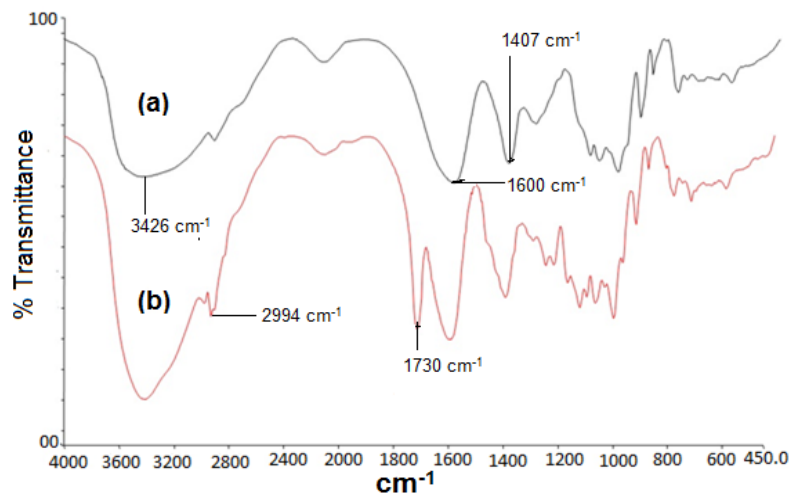


Figure 2. IR Spectra of (a) sodium alginate and (b) the graft copolymer (Alg-g-PMMA).

##### Thermogravimetric analysis (TGA)

The thermal properties of the unmodified Alginate and the graft copolymer (Alg-g-PMMA) were investigated by thermogravimetric analysis. TGA thermogram of Alginate (Figure 3) showed two steps of weight loss. The initial weight loss of about 11.27% (0.873 mg) at  $30\text{--}125^\circ\text{C}$  was due to evaporation of moisture. The second weight loss of about 33.98% (2.632 mg) in the temperature range  $200\text{--}250^\circ\text{C}$  was due to complex processes that involve breakage of C-O-C glycosidic bond, decarboxylation ( $\text{CO}_2$ ) and formation methane ( $\text{CH}_4$ ) and as reported by other researchers (Nuran and Fatma, 2013). The temperature at which 50% weight loss of the sample was found to be  $270^\circ\text{C}$ . However, in the case of Alg-g-PMMA (Figure 4), three steps of weight loss was observed. The initial weight loss of about 21.54% (1.628 mg) in the temperature range of  $200\text{--}250^\circ\text{C}$  was due to degradation of of the NaAlg backbone with release of the gases. The second weight loss of about 38.50% (2.901 mg) in the temperature range of  $300\text{--}430^\circ\text{C}$  was due to degradation of PMMA chains. The final weight loss of about 7.25% (0.546 mg) in the range of  $430\text{--}530^\circ\text{C}$  was due to decomposition of the polymer backbone with ashes as residue. On the other hand, the temperature at which 50% weight loss was found to be  $355^\circ\text{C}$  which indicates that the thermal stability of the graft copolymer is higher than that of alginate alone.

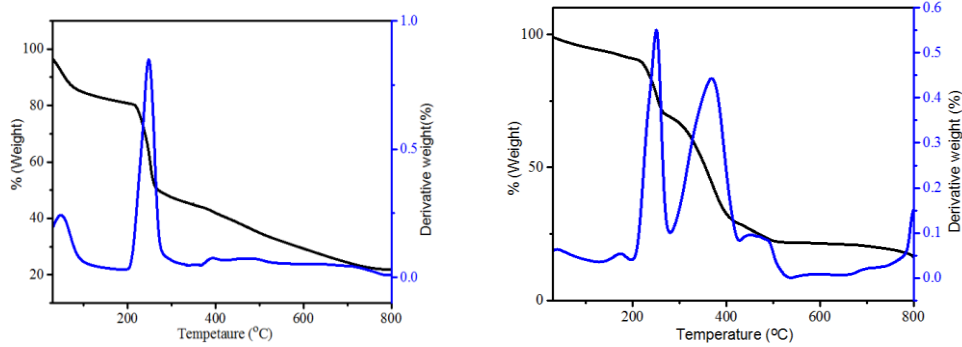


Figure 3. TGA thermogram of sodium alginate (Alg) and (b) graft copolymer (Alg-g-PMMA)

### Scanning electron microscopy

Scanning electron microscopy (SEM) is a useful tool to evaluate the surface morphology of materials. The micrograph images of the dried bead of Alg-g-PMMA and its surface morphology is shown in Figure 4. It is obvious that the surface morphology of the bead is spherical in shape with rough surfaces and porous. The diameter of the bead was found to be  $1 \text{ mm} \pm 2$  as measured by the SEM machine.

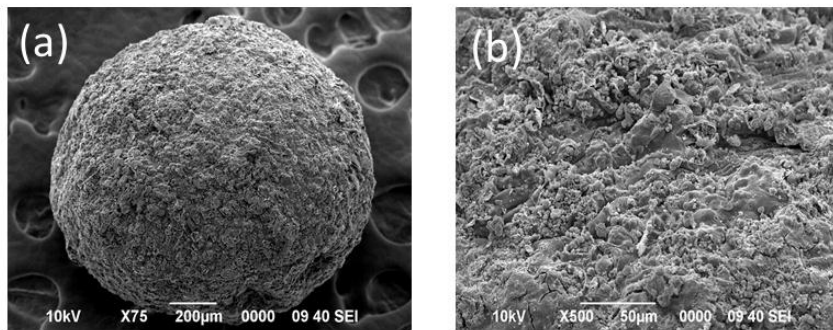


Figure 4. SEM image of (a) Alg-g-PMMA bead and (b) surface structure of Alg-g-PMMA bead.

#### 3.1.1 Effect of initial pH on adsorption of metal ions

The pH of initial solution is one of the most important factors that affect the adsorption process. Many studies have indicated that the adsorption of metal ions in batch system as well as in continuous system depends largely on pH of the solution. The adsorptive sites of the adsorbent could be primarily attributed to the carboxyl groups of alginate. It is known that the carboxyl groups tend to ionize at pH values in the range 3-4. It was found that in this study that the removal efficiency of the metal ions by the adsorbent significantly increased at pH above 3, and reached a maximum value at pH 5 for copper and cadmium ions respectively (Fig. 5).

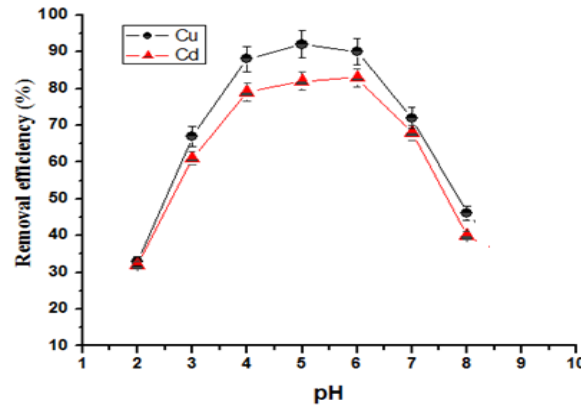


Figure 5. Effect of initial pH on the removal efficiency of metal ions by Alg-g-PMMA beads. (Initial metal concentration = 100 mg L<sup>-1</sup>, adsorbent dose = 0.1 g and contact time = 60 min)

### 3.1.2 Effect of initial metal ion concentration

The effect of initial metal ion concentration has great role in metal ion adsorption process. The removal efficiency showed a decreasing trend as the initial concentration was increased from 100 to 500 mg/L using 0.1 g adsorbent dose at optimum pH for each metal ion (Figure 6). It was observed that at 100 mg/L initial concentration removal efficiency were 98.78 and 89.50% for Cu<sup>+2</sup>, and Cd<sup>+2</sup> respectively. It is believe that at lower concentration, there would be maximum interaction between the metals ions and the binding sites of the adsorbent which lead to higher adsorption. However, the lower removal efficiency observed at higher concentrations could be due to the saturation of the adsorption sites on the adsorbent (Kumari *et al.*, 2009).

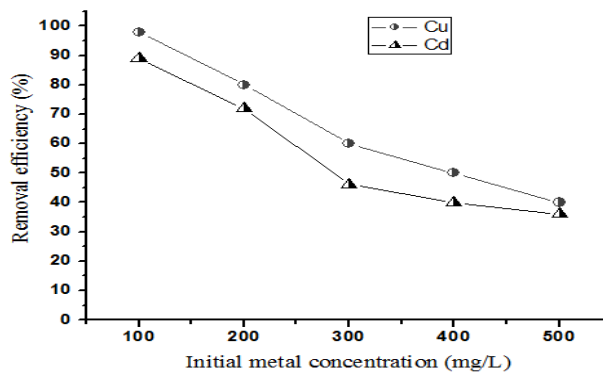


Figure 6. Effect of initial metal concentration on the removal efficiency by Alg-g-PMMA beads

## 3.2 Equilibrium isotherms studies

The equilibrium isotherm for the solid - liquid system is important for describing the adsorption behavior and also represents the relationship between the amount adsorbed by a unit of adsorbent and the amount of adsorbate remaining in the solution at equilibrium. The Langmuir and Freundlich isotherms models were selected for adsorption isotherms studies. The Langmuir model is valid for monolayer adsorption and expressed in the linear form as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b \times q_{max}} \tag{5}$$

where  $C_e$  is the equilibrium concentration (mg L<sup>-1</sup>),  $q_e$  is the amount adsorbed at equilibrium (mg g<sup>-1</sup>) per unit weight of the adsorbent;  $b$  is the Langmuir constant relating the free energy of adsorption (L



$\text{mg}^{-1}$ );  $q_{\text{max}}$  is the maximum monolayer uptake capacity of the adsorbent. The essential characteristics of the Langmuir adsorption can be expressed in terms of a dimensionless constant referred to as equilibrium parameter ( $R_L$ ), defined as:

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

The value describes the isotherm type: unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ), the adsorption is favorable (Sohn and Kim, 2005).

The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as:

$$\ln q_e = \ln K_F + n \ln C_e \quad (7)$$

Where  $K_F$  indicates adsorption capacity ( $\text{mg/g}$ ) and  $n$  an empirical parameter related to the degree of adsorption dependence on the equilibrium concentration of the metals ions. The plot  $\ln q_e$  versus  $\ln C_e$  is linear with a slope of  $1/n$  and an intercept of  $\ln K_F$  (Kumar *et al.*, 2006).

The equilibrium data fitted well to Langmuir model than Freundlich model with correlation coefficient greater than 0.99 in both cases, indicating surface homogeneity of the adsorbent and monolayer adsorption. From Langmuir model, the maximum monolayer adsorption capacity ( $q_{\text{max}}$ ) was found as 333 and 294  $\text{mg/g}$  for copper and cadmium ions, respectively.  $R_L$  values were calculated to be 0.047 and 0.101  $\text{L/mg}$  respectively thus adsorption is favorable. The Freundlich constant  $K_F$  and adsorption intensity ( $n$ ) were calculated to be 123 and 109  $\text{mg/g}$  and 0.232 and 0.432 for copper and cadmium ions, respectively. Correlation of determinations and equilibrium constants were summarized in Table 1.

**Table 1. Constants for Langmuir and Freundlich isotherms for metal ions adsorption by Alg-g-PMMA beads**

Freundlich isotherm				Langmuir isotherm		
Metal ion	Adsorption capacity ( $K_F$ ) ( $\text{mg/g}$ )	Adsorption intensity ( $n$ ) ( $\text{g/L}$ )	Correlation coefficient ( $R^2$ )	Adsorption equilibrium constant (b) ( $\text{L/mg}$ )	Adsorption capacity, ( $q_e$ ) ( $\text{mg/g}$ )	Correlation coefficient ( $R^2$ )
Cu	123	0.232	0.887	0.019	333	0.998
Cd	109	0.432	0.911	0.016	294	0.990

### 3.2.1 Kinetic studies

Kinetics of metal adsorptions governs the rate at which the adsorption is taking place as well as the efficiency of the adsorbent. The adsorption rate can vary from few seconds to several hours to reach equilibrium. The effect of contact time on the removal of metal ions is shown in Fig 7. it was observed that the adsorption equilibrium was attained in the first hour of the adsorption process. The removal efficiency of 89 % and 78 % for copper and cadmium ions were achieved within 60 minutes respectively.

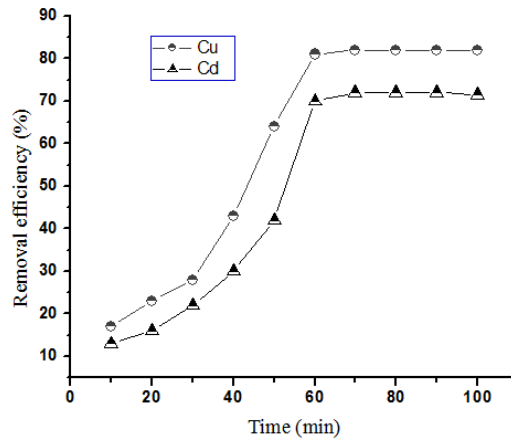


Figure 7. Effect of contact time on the removal efficiency of metal ions by Alg-g-PMMA beads.

The kinetic models of the pseudo-first order (Hoda *et al.*, 2006), (Eqn 8) and pseudo-second order (Eqn 9) proposed by Ho and McKay (Ho and McKay, 1999) were used to examine the adsorption mechanism:

$$\text{Log} (q_e - q_t) = \text{Log} q_e - \frac{k_1}{2.303} t \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

Where  $q_e$  and  $q_t$  are the amount adsorbed (mg/g) at equilibrium and at time  $t$  (min), respectively,  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo-first order rate constant and  $k_2$  ( $\text{g/mg/min}$ ) is the pseudo-second order rate constant. The  $k_1$  was calculated by plotting  $\text{Log} (q_e - q_t)$  versus  $t$  (graph not shown) and  $k_2$  was calculated by plotting  $t/q_t$  versus  $t$  (Fig. 8). The pseudo-second order equation fitted well with the experimental data. The linearity of the plot gave high coefficient of determination (0.99) and value of  $q_e$  calculated is close to the experimental data. Traditionally, the pseudo-second order model on solid-liquid adsorption systems has been commonly obtained for biosorbents [27]. Correlation coefficients and rate constant have been summarized in Table 2

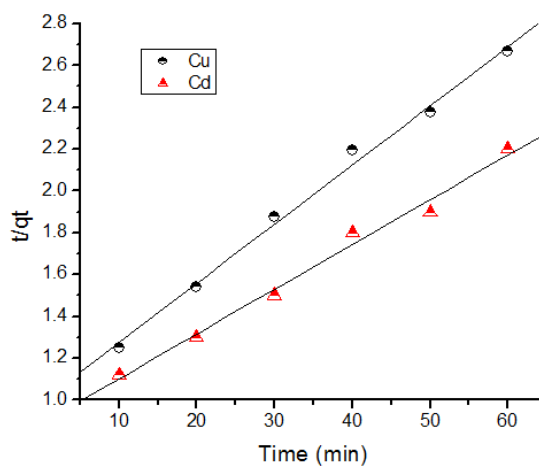


Figure 8. Pseudo-second-order kinetic plots of metal ions at 200 mg L<sup>-1</sup> concentration

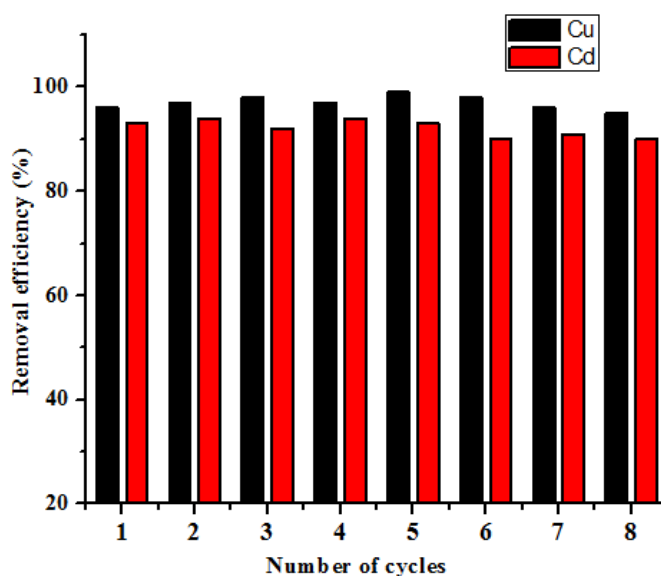


**Table 2. Kinetic rate constants and correlation coefficients for metal ions adsorption by Alg-g-PMMA beads**

Pseudo-first-order model					Pseudo-second-order model			
Metal ion	$q_{\max}$ exp. (mg/g)	$q_{\max}$ cal. (mg/g)	Rate constant $k_1$ ( $\text{min}^{-1}$ )	Correlation coefficient ( $R^2$ )	$q_{\max}$ exp. (mg/g)	$q_{\max}$ cal. (mg/g)	Rate constant $k_2$ ( $\text{g/mg/min}$ )	Correlation coefficient ( $R^2$ )
Cu	82.76	66.33	0.0351	0.8686	96.53	95.22	0.0042	0.996
Cd	63.46	54.13	0.0465	0.9708	81.72	82.44	0.0034	0.992

### 3.2.2 Adsorption-desorption cycles

To evaluate the possibility of recycling of the adsorbent, consecutive adsorption-desorption cycles were carried out for many times (Fig. 9). The process enables the adsorbed metal ions to be recovered by subsequent stripping of the metal ions from the adsorbent using dilute acids. The results showed that the adsorption capacity of the adsorbent is still good many repeated used which indicated that the adsorbent exhibited the potential application for wastewater treatment.



**Figure 9.** Adsorption-desorption cycles of the adsorbent. [ Extraction conditions: metal ion concentrations,  $100 \text{ mg L}^{-1}$ , adsorbent dose  $0.1 \text{ g}$ , batch volume  $50 \text{ mL}$ , desorption solution,  $0.1 \text{ M HNO}_3$  ( $10 \text{ mL}$ ), contact time  $1 \text{ h}$ ]

## CONCLUSION

Alg-g-PMMA beads proved to be effective adsorbent in the removal of Cu (II) Cd (II) from aqueous solutions. The adsorption was found pH depended, and was observed efficient in pH range 4-5. The kinetic data followed well with the pseudo-second order model, indicating that chemical adsorption was the rate limiting step. The Langmuir model fitted satisfactorily in isotherm adsorption equilibrium. The desorption experiments indicated that the regeneration of the adsorbent was possible for repeated usage. Thus, the prepared Alg-g-PMMA beads have potential application in wastewater treatment for the remediation of heavy metal ions.

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