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Adsorption of Cu(II) ions in aqueous solution using chitosan beads, chitosan–GLA beads and chitosan–alginate beads

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Abstract

The use of chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads, and chitosan–alginate beads for the removal of Cu(II) ions from aqueous solution at different initial pH, agitation periods, adsorbent dosage, and initial concentrations has been investigated. The equilibrium adsorption data were described by the non-linear Langmuir, Freundlich and Sips isotherms. Chitosan beads, chitosan–GLA 1:1 and 2:1 ratio beads agreed well with the non-linear Freundlich isotherm, though it gave an adsorption capacity of 64.62 mg/g, 31.20 mg/g and 19.51 mg/g, respectively, based on the non-linear Langmuir isotherm. Meanwhile, chitosan–alginate beads showed a better fit to the non-linear Langmuir isotherm giving an adsorption capacity of 67.66 mg/g. Based on the Sips isotherm, chitosan beads, chitosan–GLA 1:1 and 2:1 ratio beads are heterogeneous adsorbents, meanwhile chitosan–alginate beads is a homogeneous adsorbent. The pseudo-first and pseudo-second orders and intraparticle diffusion equation were used to evaluate the kinetic data and the constants are determined.

Keywords: Chitosan beads; Chitosan–GLA beads; Chitosan–alginate beads; Adsorption isotherm; Adsorption rates

1. Introduction

Over the years, an increase in some specific pollutants such as industrial chemicals and wastes, have contaminated water supplies and caused deterioration in the quality of drinking water. Waste streams from metal cleaning and plating facilities, mining, corrosion and electronic device manufactures may contain considerable amount of toxic and polluting heavy metals [1,2]. Among all, special attention has been given to copper. Copper is an essential nutrient in trace amount but at higher level it is toxic to plants, algae and humans. Excess copper can accumulate in the liver and can be toxic to fish at lower pH values. According to Ho et al. [3] copper plays a primary carcinogenic role among coppersmiths and the presences of Zn:Cu ratio in the soil at exceeded limits can cause stomach cancer.

Treatments for such metal-bearing effluents are chemical precipitation, membrane separation, and electrodeposition. Though such treatments are effective for the removal of heavy metals in higher concentration, there is still a necessity to develop a new method to treat waste stream with diluted amounts of heavy metals [4]. Ion exchange and reverse osmosis have showed some promising results in treating diluted metal solutions but at a higher operating cost. Thus, adsorption has become an alternative technique for the removal of heavy metal from diluted solutions. Many materials of biological origins have been used as adsorbents to remove heavy metals from water and industrial effluents [5].

Chitosan, a nitrogenous polysaccharide composed mainly of poly(β-1-4)-2-amino-2-deoxy-D-glucopyranose, is produced through the deacetylation of chitin, which is widely spread among marine and terrestrial invertebrates and in lower forms of the plant kingdom [6,7]. Chitosan is well established as an excellent natural adsorbent for metal ions due to the presences of the amino (–NH_2) and hydroxyl (–OH) groups. These groups serve as the coordination and reaction sites [8]. Apart from that, chitosan has also other useful features such as being polycationic, non-toxic, biodegradable and anti-bacterial properties [1,6,9]. Chitosan has good adsorption capability, however, due to its weak mechanical property, chemical and physical modifications are carried out on chitosan. Apart from increasing the sorption properties, physical modifications allow the expansion of the porous network due to the gel formation, which eventually decreases the crystallinity of the adsorbent. Chemical modifications also increase the sorption properties while preventing

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the dissolution of chitosan in strong acids and improving the mechanical strength of chitosan. Some of the chemical modifications may include cross-linking using a cross-linking agent, grafting of a new functional group and acetylation [10,11]. Chemical cross-linking can change the crystalline nature of chitosan and enhance the resistance of chitosan against acid, alkali and chemicals. Some of the most commonly used cross-linking agents are glutaraldehyde (GLA), epichlorohydrine (ECH) and ethylene glycol diglycidyl ether (EGDE) [12,13].

Polyelectrolytes such as alginate can also be used to complex with chitosan. Alginate is a polysaccharide biopolymer composed of anionic blocks of (1 → 4) linked α-L-gluronic acid (G) and β-D-mannuronic acid (M). Alginate (alginate salts) shows high affinity to metal ions but due to its tendency to swell in water and other mechanical weakness, its application in wastewater treatment is limited [14,15]. Alginate can be blended with chitosan to overcome the drawbacks of alginate and to combine the good characteristics of both polymers. The formation of chitosan–alginate beads is due to the strong electrostatic interaction between the amino groups of chitosan and the carboxyl groups of alginate.

The present study explores the adsorption of copper(II) ions onto chitosan beads, chitosan–GLA beads and chitosan–alginate beads. The effect of using different ratios of cross-linking agent has been studied. The influence of initial pH of copper(II) ions solution, agitation periods, adsorbent dosage and initial concentrations on the copper(II) ions uptake was studied. The non-linear Langmuir, Freundlich and Sips isotherm were used to fit the equilibrium adsorption data. The adsorption rates were determined quantitatively and compared by the pseudo-first order, pseudo-second order and intraparticle diffusion models. This information will be useful for further applications for the system design in the treatment of practical waste effluents.

2. Materials and methods

2.1. Materials

Samples of chitosan flakes with a degree of deacetylation of 65.54% (determined using an infrared spectroscopy method), were supplied by Chito-Chem (M) Sdn. Bhd., Malaysia. Glutaraldehyde (GLA) and alginic acid sodium salt from brown algae were purchased from Fluka. All the reagents used are analytical-reagent graded. Distilled water was used throughout the research.

2.2. Preparation of chitosan beads

Chitosan beads were prepared according to the same procedure described previously [2,9]. The chitosan solution was prepared by dissolving 2.00 g of chitosan flakes in 60 mL of 5% (v/v) acetic acid. The viscous solution was left overnight before adding drop wise into a 500 mL of 0.50 M NaOH. This is to ensure that the acetic acid within the chitosan gel is neutralized and to coagulate the chitosan gel to spherical uniform gel beads. The aqueous NaOH solution was under a continuous stirring. The chitosan beads were filtered, rinsed with distilled water and finally air-dried. The chitosan beads were then ground and sieved to a constant particle size (<200 μm) before use.

2.3. Preparation of chitosan–GLA beads

Chitosan–GLA beads were prepared using a similar procedure to that described previously [9]. The chitosan beads as has been prepared in Section 2.2 were used in the preparation of chitosan–GLA beads. The extensively rinsed chitosan beads were suspended in a 0.025 M or 0.050 M glutaraldehyde solution, respectively to obtain a ratio of 1:1 and 2:1 with chitosan (mol CHO:mol NH_2). The CHO group is from GLA and the NH_2 group is from chitosan. The chitosan beads were left standing for 24 h in the respective glutaraldehyde solution at room temperature. The solution was continuously stirred at an average stirring speed. The freshly prepared chitosan–GLA beads were then filtered, rinsed with hot distilled water and then followed by cold distilled water. The chitosan–GLA beads were air dried, ground and sieved to a constant particle size (<200 μm) before use. A feature that can be noticed is the intensity of color in the gel formed, as well as in the dried polymer. The spectra of colors varied from white, yellow and redbrick in the gel, to yellow to dark redbrick after drying. The intensity of the color depends on the ratio of cross-linking used.

2.4. Preparation of chitosan–alginate beads

About 2.00 g of chitosan flakes were dissolved in 60 mL of 5% (v/v) acetic acid solution. Solution of 5% (w/v) of alginic acid was prepared by mixing the fine alginic acid powder with distilled water. Both of the solutions were left standing overnight. The chitosan solution was then stirred on a hot plate stirrer at 60 °C for about 30 min. Then, the alginic acid solution was added and the mixing was continued for another 20 min at 60 °C. The blended gel solution was then dropped into a 500 mL of 0.50 M NaOH. A magnetic stirrer was used for a continuous stirring of the aqueous NaOH solution. The chitosan–alginate beads were then filtered and rinsed with distilled water to remove any NaOH residue. The beads were left to air-dry, ground and sieved to a constant particle size (<200 μm) before use.

2.5. Characterization of chitosan beads, chitosan–GLA beads and chitosan–alginate beads

Physical characteristic of chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads were determined in order to investigate the adsorption behavior of all the different types of beads. The analysis was performed using a Micromeritics ASAP 2010 gas adsorption surface analyzer. The existences of the functional groups on chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads (as shown in Fig. 1) were confirmed by a Perkin Elmer FT-IR System 2000 Model spectrometer.

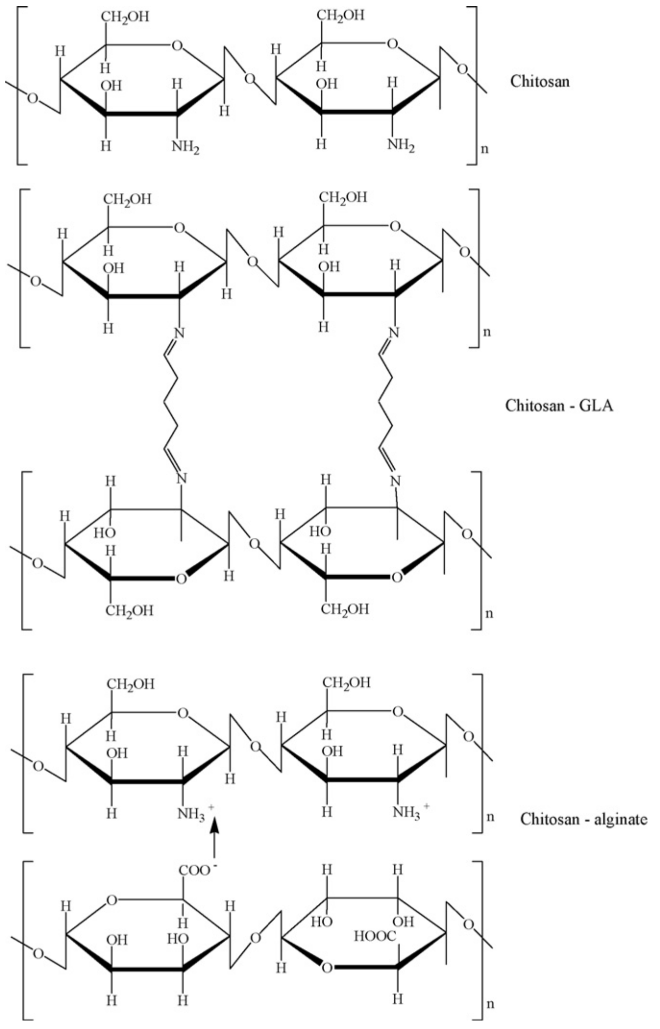

Fig. 1. Structures of chitosan beads, chitosan–GLA beads and chitosan–alginate beads.

2.6. Solubility and swelling test of chitosan beads, chitosan–GLA beads and chitosan–alginate beads

Chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads were tested with regard to their solubility in 5% (v/v) acetic acid, distilled water and 0.10 M NaOH solution. About 0.05 g of chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads were added into the three different mediums and were left stirring for 24 h.

The swelling studies for all four beads were done according to the method proposed by Denkbaş and Odabaşi [16]. About 0.05 g of chitosan beads were inserted into a tube with a diameter of 5 mm and a height of 100 mm. The level of the beads were marked before filling it up with 1 mL of 5% (v/v) acetic acid, distilled water or 0.10 M NaOH solution and were left for 24 h. After 24 h, the height of the beads in the solution was obtained. The same procedure was repeated to chitosan 1:1, 2:1 ratio beads and chitosan–alginate beads. The percentage of swelling was calculated based on the following equation [16]:

$$S = \frac{h_t - h_o}{h_o} \times 100 \qquad (1)$$

where S is the percentage of swelling, h_t is the height of swollen beads (cm) at time t and h_o is the initial height of the beads (cm).

2.7. Batch adsorption experiments

Stock solution of 1000 ppm of Cu(II) ions was prepared using the analytical reagent grade copper metal. The stock solution was diluted to give the appropriate concentrations. The batch adsorption experiments were conducted in 250 mL beakers with 50 mL of standard solutions and equilibrated using a magnetic stirrer. About 0.05 g of one of the four beads was then added into this solution and was left stirring for a certain period of time. The beakers were covered with aluminum foil. After filtration, the concentration of Cu(II) ions in the filtrate was analyzed at a wavelength of 325 nm using an atomic absorption spectrophotometer (Perkin Elmer 3100 Model).

The effect of pH on the adsorption of Cu(II) ions was studied in a pH range of 1–6. The pH of the initial 50 mL solution of 10 ppm was adjusted to the required pH value using appropriate concentrations of HCl or NaOH solutions. Chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads were equilibrated at the particular pH for about 60 min at 400 rpm. The effect of agitation period was conducted at room temperature and under the stirring rate of 400 rpm with 0.05 g of adsorbent. The effect of adsorbent dosage on the uptake of Cu(II) ions from aqueous solution was also studied. Different amounts of adsorbent from the range of 0.025–1.00 g was applied into the aqueous solution under the optimum pH and agitation period as has been determined from the previous step.

Adsorption equilibrium studies were conducted at optimum conditions and each adsorbent bead was studied under different optimum conditions. About 0.125 g of chitosan beads with a contact time of 90 min at pH 4.5 was used for the equilibrium study. Whereas, for chitosan–GLA 1:1 ratio beads and chitosan–alginate beads, a contact time of 100 min at pH 4.5 with 0.20 g of beads was applied. Finally, for chitosan–GLA 2:1, about 0.50 g of beads was required at a pH of 4.5 with 100 min of agitation period. Isotherm studies were conducted at varying initial concentration of Cu(II) ions, which was in the range of 20–300 ppm. The amount of Cu(II) ions adsorbed at equilibrium was calculated using the following equation:

$$\text{Adsorption capacity } (q_e) = \left(\frac{C_o - C_e}{W}\right) V \qquad (2)$$

where C_o is the initial concentration of Cu(II) ions (ppm), C_e is the final concentration of Cu(II) ions (ppm), V is the volume of Cu(II) ions solution (mL) and W is the weight of the chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads or chitosan–alginate beads (g) used.

The batch kinetic studies were carried out using 0.05 g of adsorbent in a 50 mL solution of 10 ppm of Cu(II) ions. After a certain period of time, the solution was filtered and the concentration of Cu(II) ions in the filtrate was determined.

Table 1
Physical characteristics of chitosan beads, chitosan–GLA beads and chitosan–alginate beads

Adsorbent	BET surface area (m^2/g)	Langmuir surface area (m^2/g)	Average pore diameter (nm)
Chitosan beads	0.33	0.50	12.86
Chitosan–GLA 1:1 ratio beads	0.41	0.62	12.70
Chitosan–GLA 2:1 ratio beads	0.52	0.80	12.81
Chitosan–alginate beads	0.29	0.45	16.32

3. Results and discussions

3.1. Characterization of chitosan beads, chitosan–GLA beads and chitosan–alginate beads

The physical property study was based on the surface area and pore size. Table 1 shows the values of BET surface area and pore diameter obtained for chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads. According to the IUPAC recommendation, total porosity can be classified into three groups according to diameter (d). The three groups are macropores ($d > 50$ nm), mesopores ($2 < d < 50$ nm) and micropores ($d < 2$ nm). Based on Table 1, it can be concluded that chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads fall into the category of mesopores. Also based on the table, it can be seen that cross-linking using GLA can increase the surface area of the adsorbents, but the chitosan–alginate beads showed much lower surface area if compared to chitosan beads.

The FTIR spectrum of the chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads are compared in Fig. 2, to determine the functional groups of all four adsorbents used for the adsorption of Cu(II) ions. Powder of the beads was mixed with spectrophotometric grade KBr in 1:10 ratio. The major peaks of the chitosan beads are located around 3400 cm^{-1} for –OH stretching vibration and 1650 cm^{-1} for –NH stretching vibration. Meanwhile, based on the spectrum of chitosan–GLA 1:1, 2:1 ratio beads, there was a significant new peak around 1660 cm^{-1}, which can be attributed to imine bond (C=N). Another new peak at 1561 cm^{-1} can be observed in the spectrum for chitosan–GLA 1:1 and 2:1 ratio beads. This is associated with an ethylenic bond (C=C) and as the density of the cross-linking was increased, the frequency of this peak increased as well. Moreover, the reduction in the intensities at 1420 cm^{-1} peak (primary amino group, $-NH_2$) showed that most of the primary amino groups were involved in the cross-linking process. The absence of the peak at 1720 cm^{-1} proves that there is no unreacted pendant aldehyde group [17].

Meanwhile, for chitosan–alginate beads, a new peak at around 1420 cm^{-1} can be seen. This peak is attributed to the $-NH_3^+$ groups of chitosan interacting with the $-COO^-$ groups of alginate. The peak appears at around 1639 cm^{-1} in the spectrum for chitosan–alginate beads can be assigned to a symmetric $-NH_3C$ deformation [18]. The peak at 1736 cm^{-1} was not found in the spectra because there is no non-ionized –COOH group in the chitosan–alginate beads [19]. The spectra confirmed that the carboxylate groups of sodium alginate were dissociated to COO^-, which formed complex with the protonated amino groups of chitosan through electrostatic interaction [18].

3.2. Solubility and swelling test of chitosan beads, chitosan–GLA beads and chitosan–alginate beads

Based on Table 2, chitosan beads were insoluble in distilled water and 0.10 M NaOH solution, but dissolves in the acetic acid solution. This is due to the protonation of the amino groups found in chitosan at a low pH. In an acidic solution, the polymer chains will fall apart and finally results in dissolution. Chemical modification on this polymer can overcome this weakness. As has been shown in Table 2, the cross-linked chitosan beads did not dissolve in all three mediums and increasing the ratio of cross-linking actually can improve the swelling effect on the

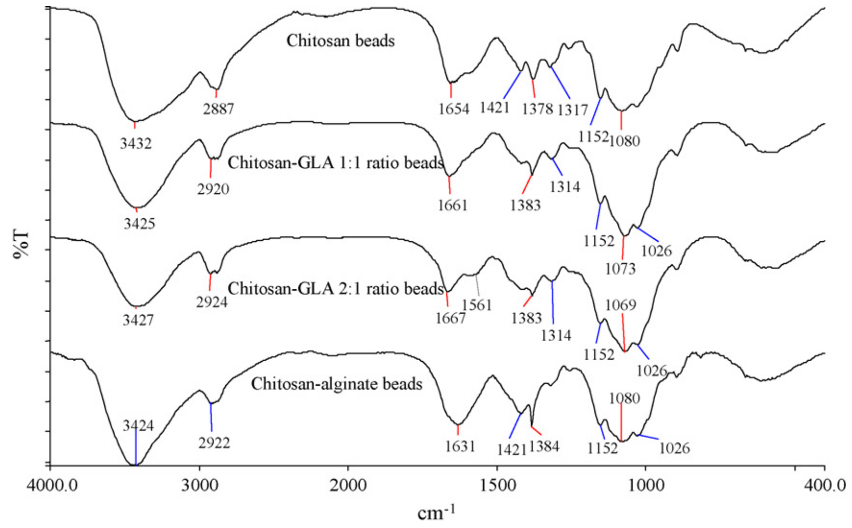

Fig. 2. FTIR spectrum of chitosan beads, chitosan–GLA beads and chitosan–alginate beads.

Table 2
Solubility effect of chitosan beads, chitosan–GLA beads and chitosan–alginate beads

Adsorbent	Solubility effect		
	5% (v/v) acetic acid	Distilled water	0.10 M NaOH
Chitosan beads	Soluble	Insoluble	Insoluble
Chitosan–GLA 1:1 ratio beads	Insoluble	Insoluble	Insoluble
Chitosan GLA 2:1 ratio beads	Insoluble	Insoluble	Insoluble
Chitosan–alginate beads	Partially soluble	Insoluble	Insoluble

adsorbent. This is due to the reaction between the primary amino groups, –NH_2 with the cross-linking agent. Thus, it reduces the number of primary amino groups that can be protonated and cause dissolution. Both of the chitosan beads and chitosan–GLA beads did not dissolve in neither neutral nor alkaline solution because the amount of H^+ present to protonate the amino groups of chitosan, were less.

Meanwhile, chitosan–alginate was partially soluble in the 5% (v/v) acetic acid solution because of the interaction between chitosan and alginate. The chitosan–alginate beads were partially soluble at a lower pH value and showed slightly higher swelling degree at pH nearly neutral, as has been shown in Table 3. According to Mi et al. [20] an increase in the swelling ability in chitosan–alginate beads at lower pH value is due to the protonation of the primary amino groups of chitosan. Meanwhile, the slightly increased swelling percentage at a neutral pH is attributed to the ionization of carboxyl groups of alginate.

The percentage of swelling as has been shown in Table 3 is important because it provides information about the crystalline nature of the adsorbent. The beads that have higher percentage of swelling are not a very good adsorbent and are very brittle. The percentage of swelling can be determined using the equation provided in Section 2.6. Based on Table 3, it can be concluded that chitosan beads is soluble in acidic medium and has a higher percentage of swelling in distilled water and alkaline medium. Meanwhile, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads showed the highest percentage of swelling in acetic acid but lower percentage of swelling in alkaline and distilled water. Cross-linking and polyelectrolyte complex can change the crystalline nature of the beads. The amount of crystalline domains in the polymer is reduced and the crystalline nature of the raw polymer is changed during the cross-linking process. This causes the matrix of the polymer to be insoluble in water and in organic solvents, but has certain degree of swelling [21]. An increase in the ratio of cross-linking used can lower the swelling percentage. As the cross-linking density increases, the hydrophilicity of the polymer is decreased due to the destruction of the crystalline structure of the polymer. Cross-linking can enhance the resistance of the polymer against acid, alkali and chemicals but it reduces the efficiency in the uptake of pollutants and adsorption capacities of the polymer.

Table 3
Swelling behavior of chitosan beads, chitosan–GLA beads and chitosan–alginate beads in different medium

Adsorbent	Percentage of swelling (%)		
	5% (v/v) acetic acid	Distilled water	0.10 M NaOH
Chitosan beads	Soluble	88.9	133.3
Chitosan–GLA 1:1 ratio beads	144.4	33.3	66.7
Chitosan–GLA 2:1 ratio beads	152.3	22.2	33.3
Chitosan–alginate beads	Partially soluble	188.9	122.2

3.3. *Effect of initial pH*

The adsorption of Cu(II) ions onto the adsorbents varies with initial pH because pH causes changes in the charge of adsorbent. In this study, the range of initial pH for Cu(II) ions adsorption study was in between pH 1 and 6. At pH values higher than 7, precipitation of Cu(II) ions as $Cu(OH)_2$ occurs simultaneously and could lead to inaccurate interpretation of adsorption. Fig. 3 shows the adsorption capacity of chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads for Cu(II) ions. As seen from Fig. 3, it is observed that the adsorption capacity of Cu(II) ions onto all the adsorbents increased with an increase in the initial pH value of the solution. The maximum adsorption of Cu(II) ions onto all four adsorbents occurred at the pH 4.5. At lower pH, the adsorption capacity of chitosan beads was low because of the dissolution of chitosan beads due to the protonation of the amino groups in the lower pH region. This reduces the number of binding sites available for the adsorption of Cu(II) ions. Moreover, the protonation of amino groups induced an electrostatic repulsion of Cu(II) cations [13]. Chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads also responded in similar manner at a very low pH due to the swelling effect of the adsorbent. If observed carefully, it can be seen that chitosan–GLA 2:1 ratio beads have a slightly higher adsorption capacity than chitosan–GLA 1:1 ratio at lower pH, due to the density of cross-linking. The higher cross-linking ratio used, it improves the swelling degree in the adsorbent and thus increases the adsorption capacity. But as the pH was increased, the chitosan–GLA 1:1 ratio beads showed a much

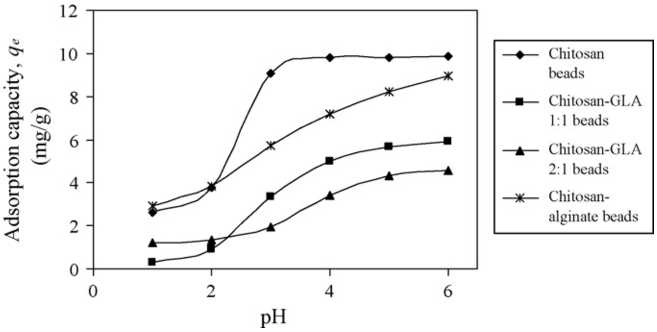

Fig. 3. Effect of initial pH on the adsorption of Cu(II) ions onto chitosan beads, chitosan–GLA beads and chitosan–alginate beads (initial Cu(II) ions concentration = 10 ppm, amount of adsorbent = 0.05 g, agitation period = 60 min, agitation rate = 400 rpm, and volume of solution = 50 mL).

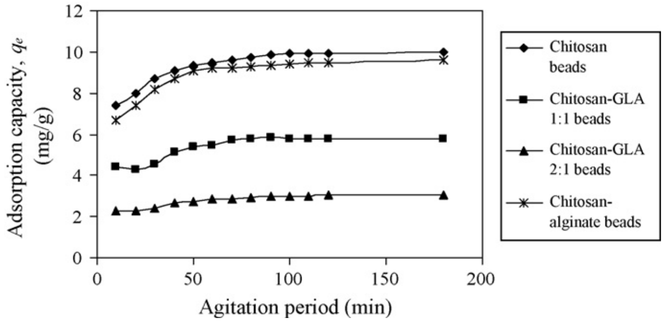

Fig. 4. Effect of agitation period on the adsorption of Cu(II) ions onto chitosan beads, chitosan–GLA beads and chitosan–alginate beads (initial pH of solution = 4.5, initial Cu(II) ions concentration = 10 ppm, amount of adsorbent = 0.05 g, agitation rate = 400 rpm, and volume of solution = 50 mL).

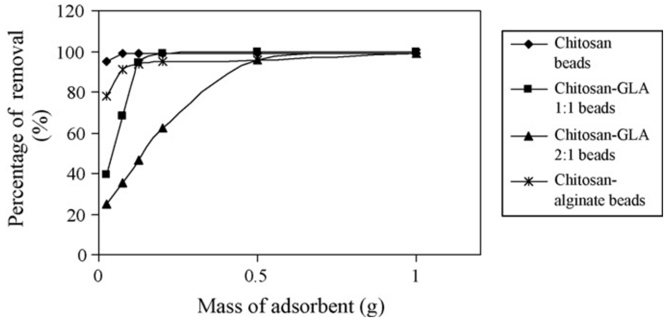

Fig. 5. Effect of adsorbent dosage on the percentage of removal of Cu(II) ions (initial pH of solution = 4.5, initial Cu(II) ions concentration = 10 ppm, agitation period = 90 min [chitosan beads], 100 min [chitosan–GLA 1:1 and 2:1 ratio beads and chitosan–alginate beads], agitation rate = 400 rpm, and volume of solution = 50 mL).

better adsorption capacity than chitosan–GLA 2:1 ratio beads because at higher degree of cross-linking and as a consequences of Schiff's base reaction, the number of amino sites available for the uptake of Cu(II) ions decreased significantly. The accessibility of sorption sites also changes due to the modification of the crystallinity of the polymer [22]. At higher pH, the adsorption of Cu(II) ions increases as the inhibitory effect of H^+ decreased with the increase in the pH. As for chitosan–alginate beads, there is an increase in the adsorption capacity as the pH of the solution increases. This indicates that Cu(II) ions are adsorbed by chitosan–alginate beads through ion-exchange with hydrogen ions on the binding sites formed by carboxyl groups on alginate [15].

3.4. *Effect of agitation period*

Agitation period is the amount of time required for an adsorption process to become constant and equilibrium is reached. It can be seen form Fig. 4 that there was a rapid uptake within the first 60 min and adsorption equilibrium was attained within 90 min for chitosan beads and 100 min for chitosan–alginate beads. Meanwhile for chitosan–GLA 1:1 and 2:1 ratio beads the adsorption equilibrium was attained at 100 min. Therefore, 90 min of contact time was chosen as the optimum contact time for chitosan beads and for chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads, a 100 min was selected. There are several parameters which determine sorption rate, like structural properties of the adsorbent (size, surface area, porosity), metal ion properties, initial concentration of metal ions, pH or chelate formation rate. Therefore, it is difficult to make a comparison between adsorbents [23].

3.5. *Effect of adsorbent dosage*

The dependence of the dosage of adsorbent used on the adsorption of Cu(II) ions was studied and the results are shown in Fig. 5. The amount of adsorbents used were varied from 0.025 g to 1.000 g while the other parameters such as pH, agitation period and agitation rate are kept constant. Based on Fig. 5, it shows that an increase in the adsorbent's dosage can increase the percentage of Cu(II) ions removal from the solution. This is expected because by increasing the adsorbent's dosage, the number of adsorption sites available for adsorbent–adsorbate interaction is increased as well. All of the adsorbent showed no further increase in the adsorption after a certain amount of adsorbent was added as has been reported by Nomanbhay and Palanisamy [24].

There will be a decrease in the adsorption capacity as has been shown in Fig. 6, which can be attributed to two reasons. An increase in the adsorbent's dosage at constant Cu(II) ions concentration and volume, will lead to unsaturation of the adsorption sites and secondly due to the particulate interaction such as aggregation resulting from high adsorbent dosage contributes to this observation. Moreover, the surface metal ions concentration (on adsorbent) and the solution metal ion concentration come to equilibrium with one another [25,26]. Based on the results obtained, further adsorption equilibrium study was conducted using 0.125 g of chitosan beads, 0.200 g of chitosan–GLA 1:1 ratio beads and chitosan–alginate beads and finally, 0.500 g of chitosan–GLA 2:1 ratio beads.

3.6. *Adsorption equilibrium isotherm*

The equilibrium isotherm is fundamental in describing the interactive behavior between the solutes and adsorbent. It is also

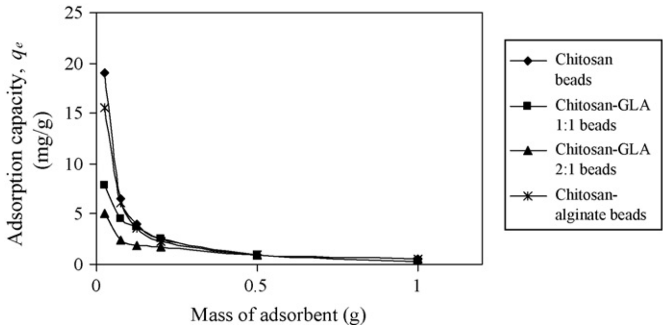

Fig. 6. Effect of adsorbent dosage on the adsorption of Cu(II) ions (initial pH of solution = 4.5, initial Cu(II) ions concentration = 10 ppm, agitation period = 90 min [chitosan beads], 100 min [chitosan–GLA 1:1 and 2:1 ratio beads and chitosan–alginate beads], agitation rate = 400 rpm, and volume of solution = 50 mL).

essential in the design of an adsorption system. Three of the most commonly used isotherm theories have been adopted in this work, namely the Langmuir, Freundlich and Sips isotherm theories. The form of Langmuir equation can be represented by the following equation:

$$q_e = \frac{bQC_e}{1 + bC_e} \quad (3)$$

where C_e is the equilibrium concentration of remaining metal ions in the solution (ppm); q_e is the amount of metal ions adsorbed per mass unit of adsorbent at equilibrium (mg/g); Q is the amount of metal ions at complete monolayer (mg/g) and b, the Langmuir constant related to the affinity of binding sites (mL/mg) and is a measure of the energy of adsorption. The model, assumes that the binding sites are homogeneously distributed over the adsorbent surface. These binding sites have the same affinity for adsorption of a single molecular layer. The bonding to the adsorption sites can be either chemical or physical but must be strong enough to prevent displacement of the adsorbed molecules [27].

The well-known Freundlich equation is presented below:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F and n are Freundlich constants indicating adsorption capacity (mg/g) and intensity, respectively. Freundlich model considers monomolecular layer coverage of solute by the adsorbent. It also assumes that the adsorbent has energetically heterogeneous surface and has different affinity for adsorption [28].

Meanwhile the Sips isotherm model can be considered as a combination of Langmuir and Freundlich equations and represented as below:

$$q_e = \frac{q_m (bC_e)^{1/n}}{1 + (bC_e)^{1/n}} \quad (5)$$

where q_m is the total number of binding sites (mg/g), b the median association constant (mL/mg) and $1/n$ is the heterogeneity factor. If the value for $1/n$ is less than one, it indicates that it is heterogeneous adsorbents, while values closer to or even one indicates that the adsorbent has relatively more homogeneous binding sites [28].

Figs. 7–10 show the non-linear plot for chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads based on non-linear Langmuir, Freundlich and Sips isotherm models. The obtained values for Langmuir and Freundlich isotherm constants and correlation coefficients are listed in Table 4 while the constants and correlation coefficient for Sips isotherm has been given in Table 5.

Based on the correlation coefficients, chitosan–beads, chitosan–GLA 1:1 and 2:1 ratio beads have a good fit to Freundlich model but chitosan–alginate beads have a better fit to Langmuir model. If all the adsorbents are compared using the non-linear Langmuir isotherm the maximum monolayer, adsorption capacity obtained for chitosan–alginate beads was the highest. The cross-linked beads showed the lowest among all four adsorbents. An increase in the density of cross-linking reduced even further the adsorption capacity. This was due to the

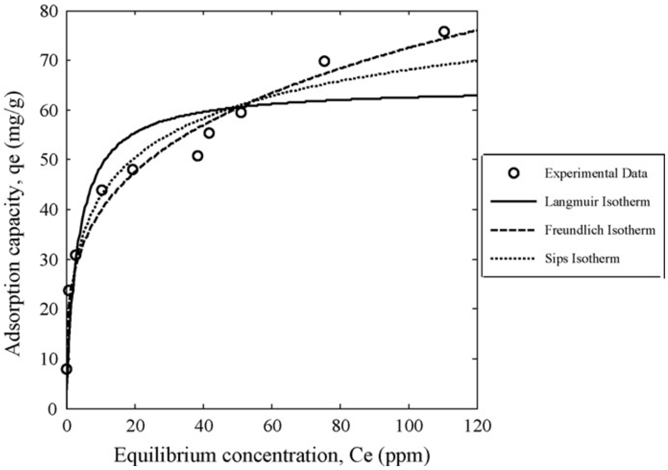

Fig. 7. Non-linear Langmuir, Freundlich and Sips isotherm for the adsorption of Cu(II) ions onto chitosan beads (initial pH of solution = 4.5, amount of adsorbent = 0.125 g, agitation period = 90 min, agitation rate = 400 rpm, and volume of solution = 50 mL).

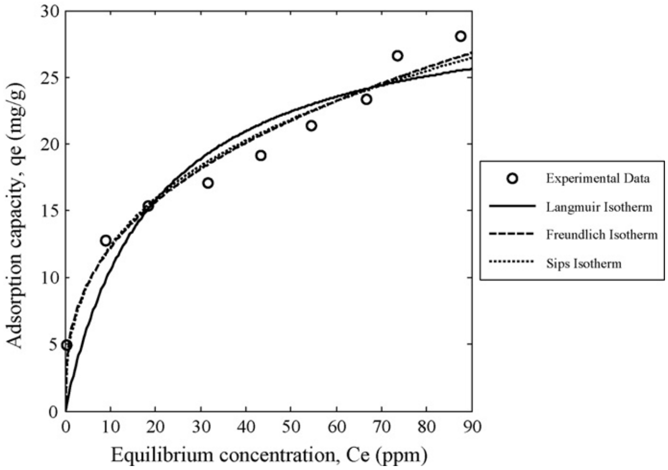

Fig. 8. Non-linear Langmuir, Freundlich and Sips isotherm for the adsorption of Cu(II) ions onto chitosan–GLA 1:1 ratio beads (initial pH of solution = 4.5, amount of adsorbent = 0.20 g, agitation period = 100 min, agitation rate = 400 rpm, and volume of solution = 50 mL).

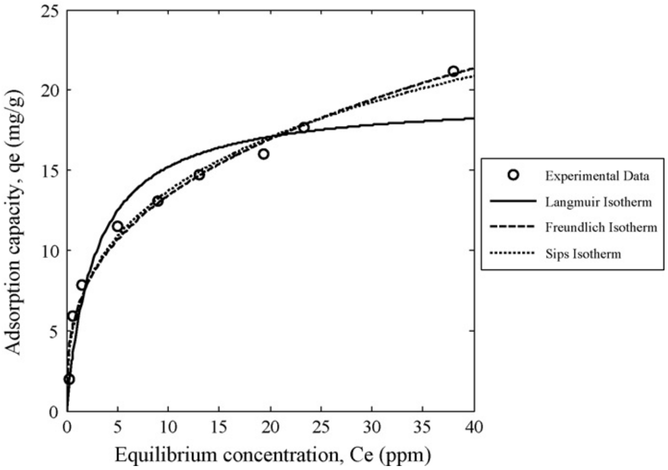

Fig. 9. Non-linear Langmuir, Freundlich and Sips isotherm for the adsorption of Cu(II) ions onto chitosan–GLA 2:1 ratio beads (initial pH of solution = 4.5, amount of adsorbent = 0.50 g, agitation period = 100 min, agitation rate = 400 rpm, and volume of solution = 50 mL).

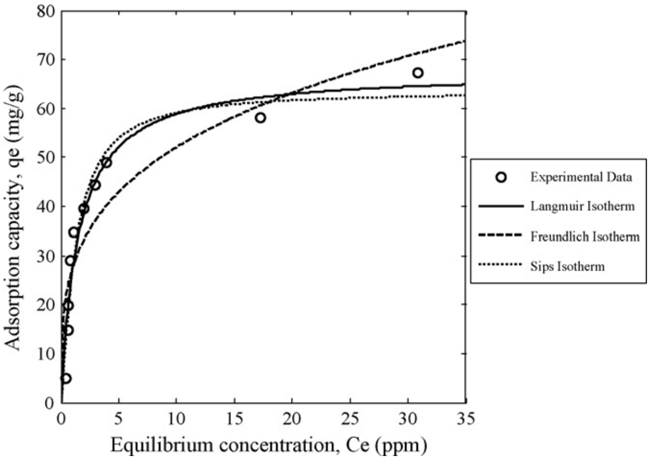

Fig. 10. Non-linear Langmuir, Freundlich and Sips isotherm for the adsorption of Cu(II) ions onto chitosan–alginate beads (initial pH of solution = 4.5, amount of adsorbent = 0.20 g, agitation period = 100 min, agitation rate = 400 rpm, and volume of solution = 50 mL).

Table 4
Langmuir and Freundlich isotherm constants and correlation coefficients for the adsorption of Cu(II) ions onto chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads

Adsorbent	Langmuir model			Freundlich model		
	Q (mg/g)	*b* (mL/mg)	*r*	K_F (mg/g)	*n*	*r*
Chitosan beads	64.62	0.30	0.9292	21.55	3.80	0.9861
Chitosan–GLA 1:1 ratio beads	31.20	0.05	0.9361	5.36	2.79	0.9838
Chitosan–GLA 2:1 ratio beads	19.51	0.35	0.9575	6.21	2.98	0.9871
Chitosan–alginate beads	67.66	0.67	0.9702	27.44	3.59	0.9061

reduced amount of amino groups that provided available sites for the uptake of Cu(II) ions. Based on the *b* values (Langmuir constant related to the affinity of binding sites), chitosan–alginate beads showed the highest affinity for Cu(II) ions. This correlates well with the highest adsorption capacity obtained for the chitosan–alginate beads.

Freundlich parameter, *n* indicates the favorability of the adsorption. If the adsorption intensity, *n* is less than one, it indicates that adsorption intensity is good (or favorable) over the entire range of concentration studied, but if the *n* value is more than one, it means that adsorption intensity is good (or favorable) at high concentration but much less at lower concentration [29]. All adsorbents showed *n* values more than one indicating that the adsorption intensity is favorable at high concentration. The K_F values can be used to indicate the relative sorption capacity of the system used. The obtained K_F values for all four adsorbents showed a similar trend as has been shown by *Q* with chitosan–alginate having the highest K_F value.

Table 5
Sips isotherm constants and correlation coefficients for the adsorption of Cu(II) ions onto chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads

Adsorbent	Sips model			
	q_m (mg/g)	*b* (mL/mg)	1/*n*	*r*
Chitosan beads	98.01	0.05	0.46	0.9790
Chitosan–GLA 1:1 ratio beads	95.23	0.001	0.43	0.9787
Chitosan–GLA 2:1 ratio beads	63.72	0.004	0.42	0.9879
Chitosan–alginate beads	63.65	0.79	1.24	0.9736

The Sips model gives a good fit for almost all the adsorbents. The calculated values for 1/*n* showed that chitosan beads, chitosan–GLA 1:1 and 2:1 ratio beads showed that these three adsorbents are heterogeneous adsorbents, while, chitosan–alginate beads is a homogeneous adsorbent. A similar observation was made by Papageorgiou et al. [28] in his study using alginate beads.

Based on the results obtained, it showed that chitosan beads, chitosan–GLA 1:1 and 2:1 ratio beads are heterogeneous adsorbents. This is because chitosan is the *N*-deacetylation product of chitin. According to Varma et al. [30], although a sharp nomenclature border does not exist between chitin and chitosan, the term “chitosan” usually represents copolymer of 2-amino-2-deoxy-D-glucopyranose and 2-acetamido-2-deoxy-D-glucopyranose where the degree of deacetylation is generally more than 60%. The presence of acetylglucosamine and glucosamine units contributes to the existence of heterogeneities in the polymer [31]. In a study carried out by Li and Bai [5], it was observed that the cross-linked chitosan–cellulose beads showed more heterogeneity in the surface properties than the chitosan–cellulose. Similarly, in this study the cross-linked chitosan–GLA beads showed more heterogeneity in the surface compared to the chitosan–alginate beads.

3.7. Adsorption kinetics

In order to investigate the mechanism of adsorption, the pseudo-first order, pseudo-second order and intraparticle diffusion model were used to study the experimental data obtained. The pseudo-first order model of Lagergren is given as [32]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{6}$$

where q_e and q_t are the amounts of Cu(II) ions adsorbed onto chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads or chitosan–alginate beads (mg/g) at equilibrium and at time *t*, respectively, and k_1 is the rate constant of first-order adsorption (min^{-1}). The straight-line plots of log ($q_e - q_t$) against *t* were used to determine the rate constant, k_1 and correlation coefficients, *r*. In many cases, the first-order equation of Lagergren does not fit well to the whole range of contact time. It would only be applicable over the initial stage of the adsorption process [33]. Fig. 11 represents the pseudo-first order plots for chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads, and chitosan–alginate beads, respectively.

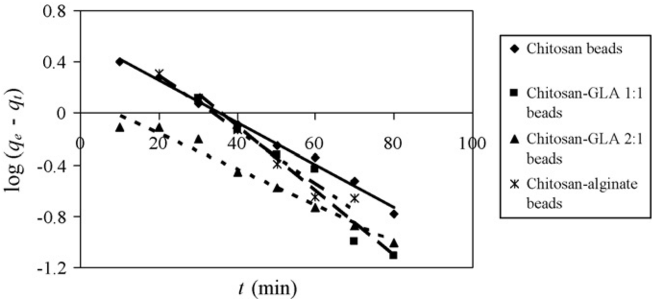

Fig. 11. Pseudo-first order plot for the adsorption of Cu(II) ions onto chitosan beads, chitosan–GLA beads and chitosan–alginate beads.

The pseudo-second order model can be expressed as [32]:

$$\frac{t}{q_\mathrm{t}} = \frac{1}{k_2 q_\mathrm{e}^2} + \frac{t}{q_\mathrm{e}} \tag{7}$$

where k_2 is the rate constant of second-order adsorption (g mg^{-1} min^{-1}). The straight-line plots of t/q_t against t were used to determine the rate constant, k_2 and correlation coefficient, r. Fig. 12 represents the pseudo-second order plots for chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads, and chitosan–alginate beads, respectively. This model is more likely to predict the adsorption behavior over the whole range of adsorption [34].

The adsorbate can be transferred from the solution phase to the surface of the adsorbent in several steps. The steps may include film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface. The overall adsorption can occur through one or more steps. The intraparticle diffusion equation is given by the equation [35]:

$$q_\mathrm{t} = k_\mathrm{int} t^{1/2} \tag{8}$$

where q_t is the amount of Cu(II) ions adsorbed onto chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads or chitosan–alginate beads (mg/g) at time t, and k_int is the intraparticle diffusion rate constant (mg g^{-1} min$^{1/2}$). The straight-line plots of q_t against $t^{1/2}$ were used to determine the intraparticle diffusion rate, k_int and correlation coefficient, r.

Fig. 13 represents the plot for the intraparticle diffusion equation for chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads, respectively. The straight-line plot for all the obtained data showed a first straight line portion which represents macropore diffusion and the second one representing micropore diffusion.

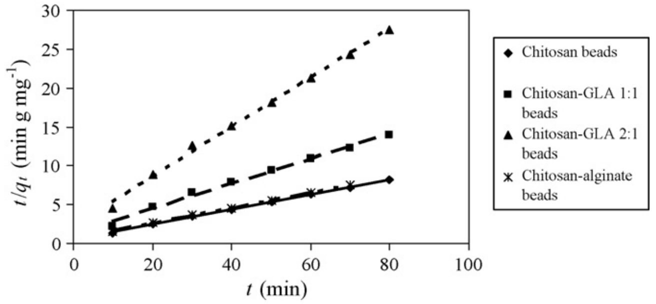

Fig. 12. Pseudo-second order plot for the adsorption of Cu(II) ions onto chitosan beads, chitosan–GLA beads and chitosan–alginate beads.

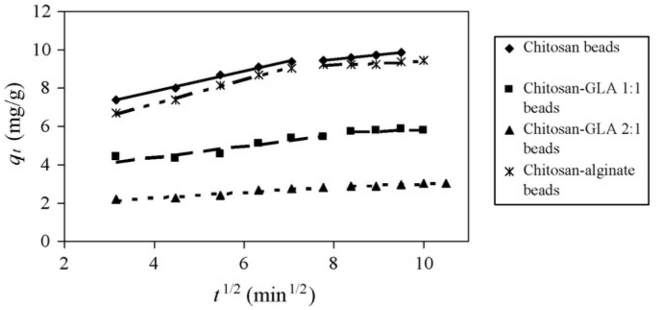

Fig. 13. Intraparticle diffusion kinetics for the adsorption of Cu(II) ions onto chitosan beads, chitosan–GLA beads and chitosan–alginate beads.

Table 6
Kinetic parameters for the adsorption of Cu(II) ions onto chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads based on the pseudo-first and pseudo-second order equation

Adsorbent	Pseudo-first order		Pseudo-second order	
	k_1 (min^{-1})	r	k_2 (g mg^{-1} min^{-1})	r
Chitosan beads	3.78×10^{-2}	0.9961	1.92×10^{-2}	0.9997
Chitosan–GLA 1:1 ratio beads	5.80×10^{-2}	0.9769	1.94×10^{-2}	0.9961
Chitosan–GLA 2:1 ratio beads	3.22×10^{-2}	0.9880	4.55×10^{-2}	0.9980
Chitosan–alginate beads	4.86×10^{-2}	0.9848	1.55×10^{-2}	0.9993

Based on Table 6, it is found that the adsorption of Cu(II) ions onto all four adsorbents follow the pseudo-second order model. The pseudo-second order assumes that chemisorptions are the rate controlling mechanism. Both of the pseudo-first and pseudo-second order could not identify the diffusion mechanism; thereby the kinetic results are analyzed using intraparticle diffusion equation.

According to Eq. (8), if the plot gives a straight line, then the adsorption is controlled solely by the intraparticle diffusion but if the adsorption data show multi-linear plots (as has been obtained in this study), it shows that there are two or more steps influencing the adsorption process [35]. If the lines pass through the origin, it indicates that intraparticle diffusion is the rate-

Table 7
Kinetic parameters for the adsorption of Cu(II) ions onto chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads based on the intraparticle diffusion equation

Adsorbents	Intraparticle diffusion equation			
	$k_{\mathrm{int},1}$ (mg g^{-1} min$^{1/2}$)	r	$k_{\mathrm{int},2}$ (mg g^{-1} min$^{1/2}$)	r
Chitosan beads	0.52	0.9937	0.24	0.9998
Chitosan–GLA 1:1 ratio beads	0.27	0.9185	0.05	0.7652
Chitosan–GLA 2:1 ratio beads	0.15	0.9535	0.069	0.9467
Chitosan–alginate beads	0.63	0.9977	0.092	0.9071

controlling step. In the present study, the slope of the first straight line was used to derive the values for $k_{\text{int},1}$ and the slope for the second one was used to obtain the $k_{\text{int},2}$ value. A trend can be seen based on Table 7 the $k_{\text{int},1} > k_{\text{int},2}$. However, as the lines did not pass the origin for all four adsorbents it shows that intraparticle diffusion is not the rate-controlling step [36,37]. Also based on the results, it can be concluded that all four adsorbents shows a very good correlation coefficient to the first portion of the straight line. This represents macropore diffusion. Moreover, the plot showed a curvature which is normally attributed to boundary layer diffusion effect or external mass transfer effects [35].

4. Conclusions

The cross-linked chitosan beads with glutaraldehyde have lower percentage of swelling and several enhanced physical properties. Chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads correspond to the category of mesoporous. In this study, the capacity of chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads were examined. Equilibrium data were fitted to non-linear Langmuir, Freundlich and Sips isotherms. Based on Langmuir isotherms, the maximum monolayer adsorption capacity for chitosan beads, chitosan–GLA 1:1, 2:1 ratio beads and chitosan–alginate beads are 64.62 mg/g, 31.20 mg/g, 19.51 mg/g and 67.66 mg/g, respectively. chitosan–GLA beads showed a lower adsorption capacity due to the cross-linking which reduces the number of amino groups available for the uptake of Cu(II) ions. The pseudo-second order best describes the adsorption process, which assumes that chemisorptions are the rate controlling mechanism. Meanwhile, based on the intraparticle diffusion equation, it can be concluded that the adsorption process follows macropore diffusion and boundary layer diffusion or external mass transfer effects. Based on the adsorption capacity obtained, a conclusion can be made that all four adsorbents can be used to treat wastewaters containing Cu(II) ions.

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