Contents lists available at ScienceDirect



Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece



# Glycine functionalized magnetic nanoparticle entrapped calcium alginate beads: A promising adsorbent for removal of Cu(II) ions



Anupama Asthana<sup>a</sup>, Renu Verma<sup>a</sup>, Ajaya Kumar Singh<sup>a,\*</sup>, Md. Abu Bin Hasan Susan<sup>b</sup>

<sup>a</sup> Department of Chemistry, Govt. V. Y. T. PG. Autonomous College, Durg, CG, India

<sup>b</sup> Department of Chemistry, Dhaka University, Dhaka, Bangladesh

#### ARTICLE INFO

Article history: Received 30 December 2015 Received in revised form 4 March 2016 Accepted 12 March 2016 Available online 15 March 2016

Keywords: Adsorption Magnetic nanoparticles Glycine functionalized Adsorption isotherms Adsorption kinetics

# ABSTRACT

Glycine functionalized magnetic nanoparticle entrapped calcium alginate beads (GFMNPECABs) were successfully prepared and used as a novel adsorbent for removal of Cu(II). The adsorbent was characterized by Fourier transform infrared (FTIR) spectroscopy, dynamic light scattering (DLS) measurements, scanning electron microscopy (SEM), x-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) surface area analysis. Magnetic nanoparticles (MNPs) could be successfully functionalized by glycine and glycine functionalized magnetic nanoparticles (GFMNPs) could be entrapped into the alginate biopolymer. BET result showed specific high surface area and mesoporous structure of the adsorbent. The adsorption capacity of GFMNPECABs for Cu(II) ions evaluated by batch adsorption experiments showed maximum value of 120 mg/g at pH 6 in 160 min. Adsorption isotherms well fitted to different available models and data could be best described by Langmuir model. The adsorption kinetics followed pseudo second order model well. The thermodynamic studies showed exothermic and spontaneous nature of Cu(II) adsorption.

© 2016 Elsevier Ltd. All rights reserved.

# 1. Introduction

The current civilization relies to a large extent on the rapid growth and development of modern industries. Development of industries has inevitably caused pollution of many different kinds, among which ground and surface water pollution has been the most detrimental one. However, despite technological advancement and prowess, the remedial measures are still in the rudimentary stage [1]. The industrial effluents contain toxic metals ions like copper which is an essential trace element for human being, but excess amount (usually higher than 1 mg/L) is very harmful. It can cause life threatening complications which inter alia, include kidney damage, hemolysis, severe vomiting [2].

Efficient technologies for effective removal of heavy metal ions from water sources are therefore critically sought for. The conventional methods such as ion-exchange, chemical oxidation/reduction, chemical precipitation, ultra-filtration, and reverse osmosis have several disadvantages like high expense, prolonged period less efficiency, production of other waste products etc.

http://dx.doi.org/10.1016/j.jece.2016.03.024 2213-3437/© 2016 Elsevier Ltd. All rights reserved. Adsorption, on the other hand has proved to be superior to other techniques because of the low-cost, simplicity of design, ease to operation, high effectiveness and possibility of reuse of the adsorbents. In the current scenario, adsorption has been very useful, promising, cost-effective and alternative for removal of copper from aqueous system [3,4].

Development of green, cheap and safe adsorbent that should have a high potential to reduce heavy metals has been a challenging task [4–6]. Magnetic sorbent technology using natural polymers has received a plethora of interest due to high efficiency and ease of separation from water by external magnetic force [5]. Iron oxide composite materials have been promising and are considered as one of the most versatile adsorbent for water purification. Iron oxides may be judiciously combined with a host material to offer high porosity and magnetic property [3,7]. The efficiency of an adsorbent is also highly dependent on the molecular structure. Surface modification can obviously enhance the capacity of adsorbent. Nanoparticles with large surface area for binding of heavy metal ions are considered intriguing in this regard, but suffers the drawback of aggregation of nanoparticles due to strong dipole-dipole attraction and their extreme small size makes the separation difficult. Polymers are recommended as a matrix for nanoparticles to ensure high mechanical, thermal

<sup>\*</sup> Corresponding author.

*E-mail addresses*: ajayaksingh\_au@yahoo.co.in, ajayaksinghau@gmail.com (A.K. Singh).

strength and chemical stability, bio-compatibility and improve hydrophobic/hydrophilic balance through nanoparticle-matrix interaction. [7–10]. Magnetic nanoparticles have so far been entrapped into various types of organic and inorganic stabilizers such as, chitosan [11–14], activated carbon [15],  $\beta$ -cyclodextrin [16,17], and alginate biopolymer [6,18,19]. Alginate, natural polysaccharide extracted from brown seaweeds, is widely used as an effective adsorbent as it is non toxic, biodegradable, inexpensive and shows the bright prospect of such materials for tuning use as an efficient adsorbent [20,21].

The present work aims at exploiting the advantageous properties of both polymer and nanoparticles in a composite material through entrapment of glycine functionalized magnetic nanoparticles in alginate beads. The GFMNPs entrapped into the alginate have been used for enhancement of the adsorption capacity, separation and recovery process due to their large surface area and presence of amino groups on the surface after glycine functionalization. The performance and efficiency of glycine functionalized magnetic nanoparticle entrapped calcium alginate beads (GFMNPECABs) as adsorbent has been evaluated and influence of system variables like time, temperature, pH has been investigated by batch method. Systematic analysis of adsorption isotherms models, kinetic results and thermodynamic parameters have been made and reusability was checked to explore the possibility of the new adsorbent for large scale industrial use for removal of Cu(II) ions from industrial effluents.

# 2. Material and methods

#### 2.1. Materials

Sodium alginate ( $C_6H_7NaO_6$ )<sub>n</sub>, ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O), ferrous chloride (FeCl<sub>2</sub>·4H<sub>2</sub>O), ammonium hydroxide (HN<sub>4</sub>OH), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Loba Chemi (Mumbai India). Calcium chloride (CaCl<sub>2</sub>), glycine ( $C_2H_5NO_2$ ), copper sulphate (CuSO<sub>4</sub>·5H<sub>2</sub>O) were received from Merck (Mumbai India). All chemicals were of analytical grade and used after further purification following standard methods. Solutions were prepared in triple distilled water.

# 2.2. Instruments

N<sub>2</sub> gas adsorption and desorption analyses of GFMNPECABs were carried out using Brunauer-Emmett-Teller (BET) analyzer (BELSORP-miniII, BEL, Japan) at constant temperature (-196°C). The dry powdered samples were pretreated for 3 h at 250 °C under N<sub>2</sub> gas to remove any surface adsorbed water or gas using a pretreatment unit (BELPREP-flowII, BEL, Japan). The specific surface area (SBET) of GFMNPECABs was calculated using the BET method. The total pore volume (V<sub>tot</sub>) was determined from the amount of N<sub>2</sub> uptake at a relative pressure  $p/p_0$  of 0.99. Pore size distribution was determined by using Barrett-Joyner-Halenda (BJH) method. Metal ion concentration was determined by using of atomic absorption spectrophotometer (AAS; Model: Varian AA-24-OFS). The particle size of bare and glycine functionalized magnetite nanoparticles were determined by dynamic light scattering (DLS) measurements (Zetasizer Nano ZS90 (ZEN3690, Malvern Instruments Ltd., UK). The prepared MNPs, GFMNPs and GFMNPECABs were characterized by X-ray diffraction (XRD) measurements were carried out with a Philips PW-1724. Morphological analyses were carried out by JEOL analytical scanning electron microscope, (Model JSM-6490LA). Samples were mounted on a round-shaped sample stage made of aluminum.

# 2.3. Synthesis of magnetic nanoparticles

Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles were synthesized by co-precipitation of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions by ammonia solution under hydrothermal conditions. First of all ferrous and ferric chloride (molar ratio 1:2) solutions with a total iron ion concentration of 0.3 M was prepared. Then 1.5 M NH<sub>4</sub>OH solution was added drop wise into the iron solution under vigorous stirring (150 rpm) maintaining pH of 10.0. Black precipitates were immediately formed, which were then heated at 80 °C for 30 min. The resulting



Fig. 1. The FTIR spectra of GFMNPs and GFMNPECABs.



Fig. 2. XRD patterns of MNPs, GFMNPs and GFMNPECABs.



Fig. 3. Particle size distribution of magnetic nanoparticles (MNPs) (a) and glycine functionalized magnetic nanoparticles (GFMNPs) (b).

nanoparticles were separated by external magnetic field and then washed several times with triple distilled water followed by heating at 250 °C under an air atmosphere for 2 h.

# 2.4. Preparation of glycine functionalized magnetic nanoparticle GFMNPs

 $Fe_3O_4$  nanoparticles were functionalized by glycine at room temperature following the procedure reported in the literature [23]. In brief, 1.0 g of magnetic nanoparticles (MNPs) was added to 0.5 mol/L glycine solution at a pH of 6.0. The mixture was well shaken for 60 min using a magnetic stirrer (150 rpm). The solid was separated by applying external magnetic field and washed once with triple distilled water. The GFMNPs were vacuum dried at room temperature.

# 2.5. Preparation of GFMNPECABs

1.5 g of sodium alginate powder was dissolved into 50 mL triple distilled water under constant stirring to form a viscous solution. Then 1.0 g of glycine modified nanoparticles was mixed well with the viscous solution. 2% calcium chloride solution was added to the prepared gel with the help of a syringe at constant stirring (100 rpm) and kept overnight for completion of gelation process to yield stable beads. Beads were washed several times with triple distilled water and stored in water for further use.



Fig. 4. N2 adsorption (open)/desorption (filled) isotherms at 77 K for GFMNPECABs (a) and pore size distribution of GFMNPECABs (b).

# 2.6. Batch adsorption experiments

Batch adsorption experiments were conducted to study Cu(II) adsorption by GFMNPECABs. Fixed amount of adsorbent and volume of metal ions solutions were taken in an Erlenmeyer flask

and shaken in thermostatic water bath shaker at different temperatures. 10 mL of 6 ppm metal ion solution was taken in Ermeyer flask then 0.1 g of GFMNPECABs was added to it and shaken (120 rpm) for 160 min at pH 6.0. The beads were separated by external magnetic field at the end of the experiment. The initial

 Table 1

 Characteristic properties of GFMNPECABs.

BET analysis of GFMNPECABs	
BET specific surface area	$27.63  \mathrm{m}^{-2}  \mathrm{g}^{-1}$
Total pore volume	$0.101  \mathrm{cm^3  g^{-1}}$
Pore size	14.64 nm
Average pore radius	2.71 nm
DLS analysis of MNPs and GFMNPs	
Average diameter MNPs	15.69 nm
Average diameter GFMNPs	78.82 nm

and final metal ion concentrations were measured using AAS. Adsorption isotherms were carried out with different concentrations and temperatures. The kinetic study of metal ion concentration was monitored at different time intervals. The removal percentage and adsorption capacity of metal ions [24] were calculated according to equations

$$\%R = \frac{C_o - C_e}{C_o} \times 100\tag{1}$$

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

$$q_t = \frac{C_o - C_t}{m} \times V \tag{3}$$

where  $C_o$  and  $C_e$  are the initial and equilibrium concentration of Cu (II) ions (mg/L) respectively,  $q_e$  is the equilibrium adsorption capacity (mg/L), *m* is the mass of adsorbent (g) and *V* is the volume of the solution (L). The  $q_t$  is the adsorption capacity at *t* time,  $C_t$  is concentration of Cu(II) ions at *t* time. The reproducibility of the results was checked by replicate measurements (at least 3) and the

consistent results with uncertainty less than 0.5% were used for analysis.

# 3. Results and discussion

# 3.1. Characterization of adsorbent

FTIR spectra of GFMNPs and GFMNPECABs with their band assignments are shown in Fig. 1. The bands at 561 and  $639 \,\mathrm{cm}^{-1}$ were attributed to Fe-O vibration mode. The same results were reflected for GFMNPs as well as for polymer beads i.e. GFMNPE-CABs. The symmetric  $(V_s)$  and asymmetric  $(V_{as})$  stretching bands of glycine COO<sup>-</sup> groups in GFMNPs appeared at 1400 and 1627 cm<sup>-1</sup>. The separation of wave number ( $\Delta = 227 \text{ cm}^{-1}$ ) for  $V_s \text{ COO}^-$  and  $V_{as}$ COO<sup>-</sup> indicated a bridging bidentate type of interaction which suggested that glycine was chemisorbed on the surface of Fe<sub>3</sub>O<sub>4</sub> NPs through carboxylate groups while amine groups remained free [25]. The GFMNPECABs showed sharp bands at 1413 and  $1609 \text{ cm}^{-1}$ . The band at  $2928 \text{ cm}^{-1}$  appeared due to Fermi interaction of NH<sub>3</sub> group with  $V_s$  of COO<sup>-</sup> and amine moeity bending mode  $\delta$ -NH<sub>3</sub> showed that NPs are coated by glycine [23]. The weak band observed at  $2856 \text{ cm}^{-1}$  was due to  $V_s$  of  $-CH_2$ group. The spectra of GFMNPs and GFMNPECABs showed same bands at identical positions of 2928 and 2856 cm<sup>-1</sup>. The band at 3418 cm<sup>-1</sup> is attributed to the —N—H stretching in GFMNPs which shifted to 3430 cm<sup>-1</sup> in case of GFMNPECABs due to formation of hydrogen bond between -N-H group in GFMNPs and -OH groups in alginate polymer. The  $V_s$  COO<sup>-</sup> and  $V_{as}$  COO<sup>-</sup> band appear at  $1413 \text{ cm}^{-1}$  and  $1609 \text{ cm}^{-1}$  in GFMNPECABs. The band at  $1627 \text{ cm}^{-1}$  for -N-H deformation band of GFMNPs shifted to 1609 cm<sup>-1</sup> in GFMNPECABs which indicated that there might be hydrogen bond and electrostatic interaction between calcium ion, GFMNPs and GFMNPECABs.

XRD patterns of MNPs, GFMNPs and GFMNPECABs reveal six characteristic peaks as shown in Fig. 2. The positions of the peaks





Fig. 5. SEM images of MNPs (a), GFMNPs(b), GFMNPECABs(c).

(b)





Fig. 6. Effect of pH on adsorption of copper by GFMNPECABs (Initial concentration 6 mg/L, temperature 313 K, adsorbent dose 10 g/L, contact time 160 min).

corresponded to  $2\theta = 30.20^{\circ}$ ,  $35.48^{\circ}$ ,  $43.21^{\circ}$ ,  $57.23^{\circ}$  and  $62.90^{\circ}$  with indices of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) for all the three samples. The peaks and intensity of the diffraction peaks indicate the Fe<sub>3</sub>O<sub>4</sub> spinel structure and no characteristic peak of impurities are detected in the XRD pattern. The XRD patterns are consistent with the standard pattern for the Joint Committee on Powder Diffraction Standards (*JCPDS*) Card No. 79–0417. The samples show broad peaks, indicating the ultra-fine nature and small crystallite size of the particles [26]. DLS was employed to determine particle size of MNPs and GFMNPs. Fig. 3 shows single peak indicating mono modal distribution of the particles. The average diameter of MNPs and GFMNPs were found to be 15.69 nm and 78.82 nm with a narrow distribution. The DLS results indicated that the GFMNPS was larger in size than pristine MNPs due to successful functionalization of MNPs by glycine.

Brunauer-Emmett-Teller (BET) method was applied for evaluation of the surface area of the adsorbent. Fig. 4(a) shows the N<sub>2</sub> adsorption and desorption behavior for GFMNPECABs at 77 K. BET specific surface area of GFMNPECABs was calculated as 27.63 m<sup>-2</sup>  $g^{-1}$ . This indicates that the surface area of the adsorbent is higher than other adsorbents [27,28]. Pore size distribution was determined by Barrett-Joyner-Halendra (BJH) model as shown in Fig. 4(b). The pore radius varies from 1 to 100 nm and the total pore volume was found to be 0.101  $\text{cm}^3 \text{g}^{-1}$  with high pore size of 14.64 nm. The sharp peak could be observed at around 4.5 nm and the average pore radius, rp was 2.71 nm. The N2 adsorptiondesorption isotherm of GFMNPECABs presented a H<sub>2</sub> type hysteresis loop, typical for mesoporous materials. The GFMNPE-CABs exhibited a better adsorption capacity with higher surface area with larger pore size. The key DLS and BET analysis results have been summarized in Table 1.

The scanning electron microscopic (SEM) images of MNPs as shown in Fig. 5 for (a) GFMNPs (b) GFMNPECABs and (c) indicated that the surface of GFMNPs were rough with a large surface area. The roughness of the surface of GFMNPECABs powder and the presence of GFMNPs on their surface could be marked. The surface morphology of beads i.e. GFMNPECABs indicated irregular structure with large surface area which enhanced the adsorption capacity of this adsorbent (vide infra). Thus the FTIR, DLS, SEM, XRD and BET results confirmed that the magnetic  $Fe_3O_4$  NPs functionaized by glycine were successfully entrapped into the polymer i.e. leads to the formation of GFMNPECABs.

# 3.2. Effect of pH

The pH of the adsorption medium is an important factor to influence the adsorption capacity of the adsorbent. Functional groups on the surface of the adsorbent are highly dependent on the pH. Adsorption of Cu(II) ions by GFMNPECABs was studied at different pH of initial metal ions as shown in Fig. 6. The pH was adjusted by using NaOH or HCl solutions. At a pH lower than 3. carboxylic groups were protonated. Therefore adsorption of Cu(II) decreases due to competition between hydrogen ions and Cu(II) ions for the binding groups [2]. Since amino groups on GFMNPs were positively charged in acidic medium, electrostatic repulsions interfere for adsorption. As pH increases carboxylic groups were quickly deprotonated and become negatively charged and electrostatic attraction between adsorbate and adsorbent favored for adsorption of Cu(II) on GFMNPECABs. At  $pH \ge 6$  amino groups on GFMNPs were non protonated and surface complexation by coordination might occur between non-protonated amine groups and Cu(II) ions [23]. If pH is higher than 6 insoluble metallic hydroxide ions (Cu(OH)<sub>2</sub>) were formed. Therefore higher pH condition is not suitable for adsorption process [29]. Calcium alginate has specific potential of ion exchange capacity between calcium ion and heavy metal ion in the solution and complexation properties [22]. At the optimum pH condition, calcium content determined in the GFMNPECABs. In initial stage Ca(II) ion concentration was found to be  $1.17 \text{ mmol g}^{-1}$ . After the completion of adsorption process Ca(II) concentration reached 0.59 mmol g<sup>-1</sup> and concentration of Cu(II) adsorbed on the beads was found to be 0.45 mmol  $g^{-1}$ . The release of Ca(II) ions into solution indicated that ion exchange mechanism was also involved in the adsorption of Cu(II) ions [20,29,30]. It can therefore be inferred that electrostatic attraction, ion exchange and surface complexation may be responsible for Cu(II) adsorption on GFMNPECABs due to entrapment of GFMNPs in the alginate polymer which provides more functional groups on the adsorbent. The probable mechanism for adsorption of Cu(II) ions by GFMNPECABs has been systematically represented in Fig. 7(a,b).

#### 3.3. Adsorption isotherms

The adsorption isotherm describes interaction between adsorbate and adsorbent under favorable condition. The equilibrium data were fitted to different theoretical models, Langmuir [31], Freundlich [32] and Temkin [33] or empirical equations for interpretation of results, evalution of parameters and prediction of adsorption mechanism and the correlation coefficient were compared to judge better fit. The adsorption capacity of GFMNPECABs for removal of Cu (II) was also determined. The adsorption isotherms were determined at  $30^{\circ}$ ,  $40^{\circ}$  and  $50^{\circ}$ C (Fig. 8).

The Langmuir model is based on homogenous surface of the adsorbent with identical and energetically equivalent adsorption sites. The linearized Langmuir isotherm model is represented as follows

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \tag{4}$$

where  $K_L$  is the Langmuir adsorption constant (L/mg) and  $Q_m$  is the maximum adsorption capacity of the adsorbent (mg/g).  $C_e$  and  $q_e$  are the equilibrium concentration and equilibrium adsorption capacity (mg/L) of Cu(II) ions. Fig. 8(a) represents  $C_e/q_e$  versus  $C_e$ .

The Langmuir isotherm model is explained using a dimension less constant separation factor or equilibrium parameter  $R_L$ , which can be calculated using equation

$$R_L = \frac{1}{1 + K_L C_o} \tag{5}$$



Fig. 7. (a) Schematic representation of probable mechanism for adsorption of Cu(II) ions by GFMNPECABs at a pH value of 6.0. (b) Schematic diagram for removal of Cu(II) ions by GFMNPECABs.

The value of  $R_L$  suggested whether the adsorption is irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ) linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ).

The Freundlich model is applied for adsorption on heterogeneous surface of adsorbent. This model describes reversible adsorption without any restriction to the formation of monolayer. The Freundlich model is expressed as

$$\log q_e = \log K_F + (1/n) \log C_e \tag{6}$$

where  $K_F$  (L/mg) and n are Freundlich constants representing the adsorption capacity and intensity of the system respectively.  $C_e$  and

 $q_e$  are the equilibrium concentration and equilibrium adsorption capacity (mg/L) of Cu(II) ions. The value of  $K_F$  and 1/n are obtained from slope and intercept of linear plot of log  $q_e$  versus log  $C_e$  shown in Fig. 8(b).

The Temkin model considers change of heat of adsorption during adsorption on the surface of adsorbent. According to this model, heat of adsorption decreased with monolayer coverage. The Temkin model given by

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{7}$$



Fig. 8. Fit of adsorption isotherms to (a) Langmuir (b) Freundlich (c) Temkin models for Cu(II) adsorption onto GFMNPECABs.

#### Table 2

Adsorption isotherm parameters for Cu(II) adsorption by GFMNPECABs at different temperatures.

Isotherm parameters	Temperature			
	40 ° C	50°C	60°C	
Langmuir				
$K_L \times 10^{-3}  (L/g)$	1.403	1.439	1.073	
$Q_m (mg/g)$	120.1	107.5	101.6	
$R_L$	0.666	0.065	0.085	
$R^2$	0.996	0.994	0.993	
Freundlich				
1/n	4.488	4.941	3.385	
$K_F$ (L/mg)	5.701	9.506	10.73	
$R^2$	0.970	0.954	0.792	
Temkin				
B <sub>1</sub>	0.166	0.138	0.156	
$K_T$ (L/mg)	78.83	130.2	37.40	
$R^2$	0.991	0.991	0.840	

where  $B_I = RT/b_r$  is temperature in K, R is universal gas constant (8.314J mol<sup>-1</sup> k<sup>-1</sup>),  $K_T$  is the equilibrium binding constant (L/mg) and  $B_I$  is related to the heat of adsorption.  $C_e$  and  $q_e$  are the equilibrium concentration and equilibrium adsorption capacity (mg/L) of Cu(II) ions. Fig. 8(c) represents plot of  $q_e$  versus ln  $C_e$ .

The equilibrium data of Cu(II) ions on GFMNPECABs were fitted to the linear form of Langmuir, Freundlich and Temkin models for the examination of the correlation coefficients ( $R^2$ ) at three different temperatures. The adsorption parameters evaluated from isotherm models are presented in Table 2. The data fitted better with Langmuir model compared to Freundlich and Temkin models at all temperatures. The maximum adsorption capacity for Cu(II) adsorption on GFMNPECABs was found to be 120 mg/g at 40 °C and 107 mg/g and 101 mg/g at 50 °C and 60 °C, respectively. Thus it could be considered as chemisorption of Cu(II) on GFMNPECABs with energetically uniform surface. The decrease in maximum adsorption capacity at higher temperatures indicated that adsorption process was exothermic in nature. The value of  $R_L$  sorption of Cu(II) at 40°, 50° and 60 °C were less than 1 and greater than 0 in all cases to indicate that Cu(II) was favorable for adsorption by GFMNPECABs. The adsorption capacity of GFMNPE-CABs was compared with some other common adsorbents summarized in Table 3 [3,29,34–38]. The adsorption capacity of GFMNPECABs was higher than other adsorbents with good adsorption capacity.

# 3.4. Kinetic studies

The effect of contact time on removal efficiency of Cu(II) by GMMNPECABs was presented in Fig. 9. Sharp removal efficiency was noticeable as the adsorption commences and gradually reaches equilibrium in first 160 min. The adsorption kinetics of Cu(II) was described by predictive theoretical models and pseudo first order and pseudo second order [39] and interaparticles diffusion models [40] were used.

Pseudo first order kinetic model is expressed by

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$
(8)

where  $q_e$  and  $q_t$  are the adsorption capacity (mg/g) at equilibrium and at time *t* (time) and  $k_1$  is the rate constant (min<sup>-1</sup>) of pseudo

#### Table 3

Comparison of adsorption capacity of GFMNPECABs with other common adsorbents.

Adsorbents	Q <sub>m</sub> (mg/g)	References
GFMNPECABs	120	present
		study
Amino-functionalized magnetic nanoparticles	28.7	[34]
Chitosan cellulose hydrogel beads	53.2	[35]
Chitosan coated sand	8.18	[29]
Modified chitosan transparent thin membrane	8.414	[36]
Calcium alginate immobilized kaolin	53.63	[37]
Calcium alginate encapsulated magnetic sorbent	60	[3]
Glutaraldehyde cross linked humic acid immobilized sodium alginate porous membrane	116.41	[38]

Table 4

Kinetic parameters of different models for Cu(II) adsorption by GFMNPECABs at different temperatures.

Kinetic parameters	Temperature			
	25°C	30°C	40 °C	50°C
Pseudo-first-order				
$k_1 ({ m min}^{-1})$	0.023	0.016	0.018	0.013
$R^2$	0.978	0.961	0.945	0.855
Pseudo-second-order				
$k_2 (g m g^{-1} m i n^{-1})$	0.177	0.146	0.175	2.847
$R^2$	0.992	0.997	0.998	0.989
Intra-particle diffusion				
A (mg/g)	0.268	0.368	0.307	0.475
k <sub>id</sub> (mg/gmin)	0.002	0.017	0.022	0.008
$R^2$	0.927	0.927	0.820	0.897

first order adsorption. The rate constant  $(k_1)$  was determined from slope. The plot of log  $(q_e-q_t)$  versus t was shown in Fig. 9(a). Pseudo second order kinetic model is given by

r seudo second order kinetic moder is given by

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

where  $q_e$  and  $q_t$  are the adsorption capacity (mg/g) at equilibrium and at time t (time),  $k_2$  (g/g per min) is the rate constant. The values of  $k_2$  and  $q_e$  were calculated from the slope and intercept of the plot of  $t/q_t$  versus t as presented in Fig. 9(b). Intraparticles diffusion model suggested that adsorption of metals onto adsorbent may be controlled via external film diffusion while the final part may be the intraparticles diffusion as rate controlling step. This model is represented by

$$q_t = K_{id}\sqrt{t} + A \tag{10}$$

where  $q_t$  is the adsorption capacity (mg/g) at t time (min),  $K_{id}$  is the diffusion rate constant (mg/g min<sup>1/2</sup>) and A (mg/g) is constant. Fig. 9(c) showed the linear plots of  $q_t$  versus  $t^{1/2}$ .

The values of the parameters of kinetic models are listed in Table 4. The correlation coefficients have been compared with pseudo first order, pseudo second order and interaparticle



Fig. 9. Adsorption kinetic data plots of Cu(II) by GFMNPECABs at different temperatures (a) pseudo first order (b) pseudo second order and (c) intraparticle diffusion models for Cu(II) adsorption by GFMNPECABs.

t<sup>1/2</sup> (min <sup>1/2</sup>)



**Fig. 10.** Van't Hoff's plot to determine thermodynamic parameters for removal of Cu (II) by GFMNPECABs.

diffusion models at four different temperatures. Furthermore pseudo second order kinetic model showed good agreement with excellent correlation coefficients greater than 0.99 at all temperatures to indicate that the chemisorptions has been the rate controlling step for Cu(II) adsorption onto GMMNPECABs. The correlation coefficients of pseudo first order kinetics and intraparticle diffusion models were slightly lower and might not be the rate limiting step.

# 3.5. Thermodynamic studies

The thermodynamic parameters for the adsorption process such as Gibbs free energy change ( $\Delta G^{\circ}$ ), enthalpy change ( $\Delta H^{\circ}$ ) and entropy change ( $\Delta S^{\circ}$ ) were calculated by using following equations [27].

$$K_c = \frac{C_A}{C_B} \tag{11}$$

$$\Delta G^{\circ} = -RT \ln K_c \tag{12}$$

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(13)

where  $K_c$  is the equilibrium constant  $C_A$  and  $C_B$  are the concentration on the adsorbate on the adsorbent and residual concentration at equilibrium, respectively.  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  represent change in the Gibbs free energy (kJ mol<sup>-1</sup>), enthalpy change (kJmol<sup>-1</sup>) and entropy change (J mol<sup>-1</sup> K). *T* is temperature in Kelvin (K). The value of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  were calculated from slope and intercept of a plot of  $K_c$  versus 1/T (Fig. 10). The  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  evaluated as -18.39 kJ mol<sup>-1</sup> and 34.42 Jmol<sup>-1</sup> k<sup>-1</sup>, respectively. The negative value of enthalpy indicated exothermic nature of Cu (II) adsorption and positive value of enthalpy change suggested that increase in randomness of GFMNPECABs and metal solution. The value of  $\Delta G^{\circ}$  was calculated -8203.2, -7740.9 and -7519.4 kJ mol<sup>-1</sup> for  $40^{\circ}$ ,  $50^{\circ}$  and  $60^{\circ}$ C, respectively that showed adsorption of Cu(II) on GFMNPECABs was thermodynamically feasible and spontaneous at all temperatures.

## 3.6. Desorption and reusability study

The recovery of adsorbent is crucial factor for economic feasibility and for proper disposal. Desorption of Cu(II) ions from GFMNPECABs was performed using 0.2 M HNO<sub>3</sub> solution. The reusability of the adsorbent was found up to three successive



Fig. 11. Performance of GFMNPECABs through multiple regeneration cycles.

cycles of adsorption-desorption (Fig. 11). The adsorption and desorption cycle could be performed retaining good adsorption capacity. In the fourth cycle, however, mass loss of the beads was marked due to the use of acid for regeneration to bring about decreased in the maximum adsorption capacity. Under acidic condition, the amino groups of GFMNPs render in to the form of  $-NH_3^+$  to cause possible weight loss in repeated runs.

#### 4. Conclusion

Glycine functionalized magnetic nanoparticle entrapped calcium alginate beads were quite effective for removal of Cu(II) ions from aqueous solution. GFMNPs could be successfully prepared and then entrapped into the alginate biopolymer. The GFMNPACABs showed mesoporous structure with high specific surface area. The modification of MNPs provides amine groups as coordinating group for Cu(II) ions. The adsorption isotherms followed Langmuir model with maximum adsorption capacity of 120 mg/g in 160 min at a pH of 6.0. The adsorption kinetic data fitted to pseudo second order model. The mechanism of Cu(II) adsorption by GFMNPACABs involves surface complexation by coordination possibility between non-protonated amine groups and Cu(II) ions. Electrostatic attraction might also be present between carboxylate groups and Cu(II) ions. The free energy and enthalpy changes indicated spontaneous and exothermic nature of Cu(II) adsorption by GFMNPACABs with good reusability and magnetic separation. The results suggested that GFMNPACABs exhibited good adsorption potential towards heavy metal ions. This will open up new route for efficient removal of heavy metal ions from using a biodegradable and environmentally benign adsorbent. Work is now underway to exploit the potential to real samples and to assess the economical viability for a wide range of effluent treatments.

# **Conflict of interest**

None.

#### Acknowledgement

A. Asthana is thankful to University Grants Commission (UGC) regional office Bhopal, Madhya Pradesh (M. P.) India for minor research grants.

# References

[1] W.S. Tan, A.S.Y. Ting, Efficacy and reusability of alginate-immobilized live and heat-inactivated Trichoderma asperellum cells for Cu(II) removal from aqueous solution, Bioresour. Technol. 123 (2012) 290–295.

- [2] W.S. Tan, A.S.Y. Ting, Alginate-immobilized bentonite clay: adsorption efficacy and reusability for Cu(II) removal from aqueous solution, Bioresour. Technol. 160 (2014) 115–118.
- [3] S.F. Lim, Y.M. Zheng, S.W. Zou, J.P. Chen, Removal of copper by calcium alginate encapsulated magnetic sorbent, Chem. Eng. J. 152 (2009) 509–513.
- [4] X.T. Zhao, T. Zeng, X.Y. Li, Z.J. Hu, H.W. Gao, Z. Xie, Modeling and mechanism of the adsorption of copper ion onto natural bamboo sawdust, Carbohydr. Polym. 89 (2012) 185–192.
- [5] P.E. Podzus, M.V. Debandi, M.E. Daraio, Copper adsorption on magnetiteloaded chitosan microspheres: a kinetic and equilibrium study, Physica B 407 (2012) 3131–3133.
- [6] A. Idris, N.S.M. Ismail, N. Hassan, E. Misran, A.F. Ngomsik, Synthesis of magnetic alginate beads based on maghemite nanoparticles for Pb(II) removal in aqueous solution, J. Ind. Eng. Chem. 18 (2012) 1582–1589.
- [7] Y. Yao, S. Miao, S. Yu, L.P. Ma, H. Sun, S. Wang, Fabrication of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> core/ shell nananoparticles attached to graphene oxide and its use as an adsorbent, J. Coll. Interface Sci. 379 (2012) 20–26.
- [8] X. Zhao, L. Lv, B. Pan, W. Zhang, S. Zhang, Q. Zhang, Polymer-supported nanocomposites for environmental application: a review, Chem. Eng. J. 170 (2011) 381–394.
- [9] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C. Huang, G.X. Xie, Z.F. Liu, Use of iron oxide nanomaterials in wastewater treatment: a review, Sci. Total Environ. 424 (2012) 1–10.
- [10] M. Hua, S. Zhang, B. Pan, W. Zhang, L. Lv, Q. Zhang, Heavy metal removal from water/wastewater by nanosized metal oxides: a review, J. Hazard. Mater. 211– 212 (211) (2012) 317––.
- [11] L. Zhou, Y. Wang, Z. Liu, Q. Huang, Characteristics of equilibrium, kinetics studies for adsorption of Hg(II)Cu(II), and Ni(II) ions by thiourea-modified magnetic chitosan microspheres, J. Hazard. Mater. 161 (2009) 995–1002.
- [12] H.V. Tran, L.D. Tran, T.N. Nguyen, Preparation of chitosan/magnetite composite beads and their application for removal of Pb(II) and Ni(II) from aqueous solution, Mater. Sci. Eng. C 30 (2010) 304–310.
- [13] L. Zhou, Z. Liu, J. Liu, Q. Huang, Adsorption of Hg(II) from aqueous solution by ethylenediamine-modified magnetic crosslinking chitosan microspheres, Desalination 258 (2010) 41–47.
- [14] M.M. Lakouraj, F. Hasanzadeh, E.N. Zare, Nanogel and super-paramagnetic nanocomposite of thiacalix[4] arene functionalized chitosan: synthesis, characterization and heavy metal sorption, Iran. Polym. J. 23 (2014) 933–945.
- [15] L.H. Ai, H.Y. Huang, Z.L. Chen, X. Wei, J. Jiang, Activated carbon/CoFe<sub>2</sub>O<sub>4</sub> composites: facile synthesis, magnetic performance and their potential application for the removal of malachite green from water, Chem. Eng. J. 156 (2010) 243–249.
- [16] A.Z. Badruddoza, M.T. Rahman, S. Ghosh, M.Z. Hossain, J.Z. Shi, K. Hidajat, M.S. Uddin, β-Cyclodextrin conjugated magnetic, fluorescent silica core-shell nanoparticles for biomedical applications, Carbohydr. Polym. 95 (2013) 449– 457.
- [17] X.B. Zhang, Y. Wang, S.T. Yang, Simultaneous removal of Co(II) and 1-naphthol by core-shell structured Fe<sub>3</sub>O<sub>4</sub>@cyclodextrin magnetic nanoparticles, Carbohydr. Polym. 114 (2014) 521–529.
- [18] A.N. Bezbaruah, S. Krajangpan, B.J. Chisholm, E. Khan, J.J.E. Bermudez, Entrapment of iron nanoparticles in calcium alginate beads for groundwater remediation applications, J. Hazard. Mater. 166 (2009) 1339–1343.
- [19] M.M. Lakouraj, F. Mojerlou, E.N. Zare, Nanogel and superparamagnetic nanocomposite based on sodium alginate for sorption of heavy metal ions, Carbohydr. Polym. 106 (2014) 34–41.
- [20] A. Bee, D. Talbot, S. Abramson, V. Dupuis, Magnetic alginate beads for Pb(II) ions removal from wastewater, J. Coll. Interface Sci. 362 (2011) 486–492.

- [21] E.N. Zare, M.M. Lakouraj, M. Mohseni, A. Motahari, Multilayered electromagnetic bionanocomposite based on alginic acid: characterization and biological activities, Carbohydr. Polym. 130 (2015) 372–380.
- [22] Y. Li, F. Liu, B. Xia, Q. Du, P. Zhang, D. Wang, Z. Wang, Y. Xia, Removal of copper from aqueous solution by carbon nanotube/calcium alginate composites, J. Hazard. Mater. 177 (2010) 876–880.
- [23] N.C. Feitoza, T.D. Goncalves, J.J. Mesquita, J.S. Menegucci, M.K.M.S. Santos, J.A. Chaker, R.B. Cunha, A.M.M. Medeiros, J.C. Rubim, M.H. Sousa, Fabrication of glycine-functionalized maghemite nanoparticles for magnetic removal of copper from wastewater, J. Hazard. Mater. 264 (2014) 153–160.
- [24] B. Liu, X. Lv, X. Meng, G. Yu, D. Wang, Removal of Pb(II) from aqueous solution using dithiocarbamate modified chitosan beads with Pb(II) as imprinted ions, Chem. Eng. J. 220 (2013) 412–419.
- [25] K.C. Barick, P.A. Hassan, Glycine passivated Fe<sub>3</sub>O<sub>4</sub> nanoparticles for thermal therapy, J. Coll. Interface Sci. 369 (2012) 96–102.
- [26] G.L. Li, Y.R. Jiang, K.L. Huang, P. Ding, I.I. Yao, Kinetics of adsorption of sacharomyces cereviceae mandelated dehydrogenase on magnetic Fe<sub>3</sub>O<sub>4</sub>chitosan nanoparticles, J. Coll. Interf. Sci. A 320 (2008) 11–18.
- [27] K.Y. Kumar, H.B. Muralidhara, Y.A. Nayaka, J. Balasubramanyam, H. Hanumanthappa, Low-cost synthesis of metal oxide nanoparticles and their application in adsorption of commercial dye and heavy metal ion in aqueous solution, Powder Technol. 246 (2013) 125–136.
- [28] M. Thirumavalavan, Y.L. Lai, J.F. Lee, Cellulose-based native and surface modified fruit peels for the adsorption of heavy metal lons from aqueous solution: langmuir adsorption isotherms, Chem. Eng. J. 56 (2011) 2249–2255.
- [29] M.W. Wan, C.C. Kan, B.D. Rogel, M.L.P. Dalida, Adsorption of copper (II) and lead (II) ions from aqueous solution on chitosan coated sand, Carbohydr. Polym. 80 (2010) 891–899.
- [30] A.F. Ngomsik, A. Bee, J.M. Siaugue, V. Cabuil, G. Cote, Nickel adsorption by magnetic alginate microcapsules containing an extractant, Water Res. 40 (2006) 1848–1856.
- [31] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids, J. Am. Chem. Soc. 38 (1916) 2221–2295.
- [32] H. Freundlich, Uber die adsorption in losungen, Z. Phys. Chem. 57 (1906) 85-470.
- [33] M.I. Tempkin, V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catalyst, Acta Phys. Chim. Sin. 12 (1940) 327–356.
- [34] H. Li, D.I. Xiao, H. He, R. Lin, P.L. Zuo, Adsorption behavior and adsorption mechanism of Cu (II) ions on amino-functionalized magnetic nanoparticles, Trans. Nonferrous Met. Soc. China 23 (2013) 2657–2665.
- [35] N. Li, R. Bai, Copper adsorption on chitosan cellulose hydrogel beads: behaviors and mechanisms, Separ. Purif. Method. 42 (2005) 237–247.
- [36] Z. Cheng, X. Liu, M. Han, W. Ma, Adsorption kinetic character of copper ions onto a modified chitosan transparent thin membrane from aqueous solution, J. Hazard. Mater. 182 (2010) 408–415.
- [37] Y. Li, B. Xia, Q. Zhao, F. Liu, P. Zhang, Q. Du, D. Wang, D. Li, Z. Wang, Y. Xia, Removal of copper ions from aqueous solution by calcium alginate immobilized kaolin, J. Environ. Sci. 23 (2011) 404–411.
- [38] J.H. Chen, Q.L. Liu, S.R. Hu, J.C. Ni, Y.S. He, Adsorption mechanism of Cu(II) ions from aqueous solution by glutaraldehyde cross linked humic acid-immobilized sodium alginate porous membrane adsorbent, Chem. Eng. J. 173 (2011) 511–519.
- [39] A.E. Nemr, Potential of pomegranate husk carbon for Cr(VI) removal from waste water: kinetic and isotherm studies, J. Hazard. Mater. 161 (2009) 132– 141.
- [40] F.C. Wu, R.L. Tseng, R.S. Juang, Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics, Chem. Eng. J. 153 (2009) 1–8.