

Removal of cadmium from aqueous solution using modified magnetic glycine modified cross-linked chitosan resin

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ARTICLE INFO

Article History:

Received: Jan. 5, 2021

Accepted: Jan. 24, 2021

Online: Feb. 7, 2021

Keywords:

Magnetic modified
Cadmium removal,
magnetite,
chitosan,
adsorption isotherm

ABSTRACT

In the present study, the adsorption of Cd(II) ions onto magnetic glycine modified crosslinked chitosan (MGMCR) resin has been investigated. Batch experiments were performed to study the effect of some parameters such as the initial Cd(II) concentration, pH value of the solution, adsorbent dose and the contact time on the adsorption process. The optimal pH for the adsorption of Cd(II) was found to be at 5 and the equilibrium was accomplished within 120 minutes. The result obtained from equilibrium adsorption studies are fitted in Langmuir and Freundlich adsorption models and the data was found to agree well with the Langmuir model. The maximum uptake was found to be 172 mg g⁻¹ at 25 °C at pH 5.

INTRODUCTION

Water is the most vital substance for life on the earth and a precious resource for human civilization for many critical areas such as: food, energy, industrial, and the environment. Water resources are increasingly decreasing and need to be preserved. In recent years, industrialization, agricultural activities, rapid population growth and urbanization have contributed negatively to clean water resources (Ali *et al.*, 2018; Basheer, 2018). Different pollutants such as pharmaceuticals, pesticides, dyes and heavy metals have contaminated the water resources. Presence of these contaminants in aqueous environments is environmentally hazardous for human beings and animals. Among these pollutants, heavy metal is one of the most hazardous species, due to their toxic nature especially when their concentrations exceed the allowable limits in the ecosystem. These pollutants are non-biodegradable and can be absorbed by marine life. Once high concentrations of heavy metals enter the food chain, they tend to accumulate in living tissues and thus, dysfunction the system of the human bodies (Fu, 2011).

Different treatment methods have been developed to remove heavy metals, which include chemical precipitation, solvent extraction, ion exchange, evaporation, reverse osmosis, electrolysis and adsorption. However, most of these methods tend to show some economical and technical disadvantages (**Mehdinia *et al.*, 2015**). For example, chemical precipitation has been widely used to remove dyes or heavy metals from inorganic effluent by increasing the pH of the solution to convert the soluble substances into an insoluble form (**Mehdinia *et al.*, 2015**). Even the process is simple, it generates a large quantity of sludge which requires further treatment and high cost.

Adsorption using low-cost natural adsorbents such as agricultural wastes, clay materials and seafood processing wastes is one of the few promising alternatives which can be applied to wastewaters with low concentrations of heavy metal ions (**Juang and Shao, 2002**).

Chitosan (CS) is well established as an excellent natural adsorbent biopolymer it is efficient, inexpensive, biodegradable, nontoxic, and environmentally friendly (**Ngah *et al.*, 2011**, **Nguyen *et al.*, 2013**). CS molecules contain a substantial number of reactive hydroxyl (-OH) and amino (-NH₂) groups that can coordinate to toxic pollutants to form complexes with various heavy metal ions. However, the disadvantage of this sorbent when used directly as an adsorbent is its weak acid resistance (i.e., quite soluble in acidic solutions), prone to swelling, weak mechanical stability and small adsorption capacity for certain metal ions (**Kuang *et al.*, 2013**; **Mi *et al.*, 2015**). To enhance its stability under acidic conditions, cross-linking and solid particle coupling treatments for CS are commonly employed (**Hu *et al.*, 2011**). The cross-linking procedure may be performed by reaction of chitosan with different reagent such as epichlorhydrin (ECH) (**Chen *et al.*, 2008**) and glutaraldehyde (**Zhang *et al.*, 2011**). Though cross-linking reduces the adsorption capacity, but it will increase the stability of the polymer.

Magnetic modified chitosan resins represent an important class of promising adsorbents as they are highly selective, efficient and easily regenerable relative to other types of adsorbent (**Monier *et al.*, 2010**; **Elwakeel, 2009**). These magnetic resins is easily collected from aqueous media using an external magnetic field and displayed higher uptake capacity compared to the magnetic particles-free resin. However, since Chang and Chen reported the CMCS-MNP sorbent in 2005 (**Chang and Chen, 2005**), many magnetic chitosan has employed for different functions as theranostic applications (**Baktask *et al.*, 2020**; **Lian *et al.*, 2020**) and some studies (**Kuang *et al.*, 2013**; **Mi *et al.*, 2015**; **Song *et al.*, 2016**, **Nuryono *et al.*, 2020**) have focused on its sorption of heavy metals from aqueous solutions.

Cadmium pollution of the environment has become a serious problem due to the increasing consumption of cadmium by industry in the past 20 years. Cadmium is introduced into the environment from the effluence of electroplating industry, and in solid and aqueous discharges from mining operations. Cd(II) toxicity usually occurs through

oral intake and inhalation (Nogami *et al.*, 2000), affecting organs of the body, such as the liver, kidney, central nervous system, immune system, and blood (Bernard and Lauwerys, 1984).

In this study, we attempted to use the magnetite-crosslinked glycine modified chitosan (MCGC) biopolymer for the adsorption of cadmium ions in aqueous solution. The important physicalchemical properties of MCGC were characterized. A series of adsorption experiments were performed. The pH influence, kinetics and equilibrium of the cadmium ions onto MCGC beads were studied and some important adsorption parameters have been obtained.

MATERIALS AND METHODS

2.1. Materials

Chitosan (from crab shell), glycine, glutaraldehyde, isopropyl alcohol, epichlorohydrin, cadmium acetate dihydrate were Aldrich products. All other chemicals were Prolabo products and were used as received.

2.2 Preparation of magnetic glycine modified chitosan resin

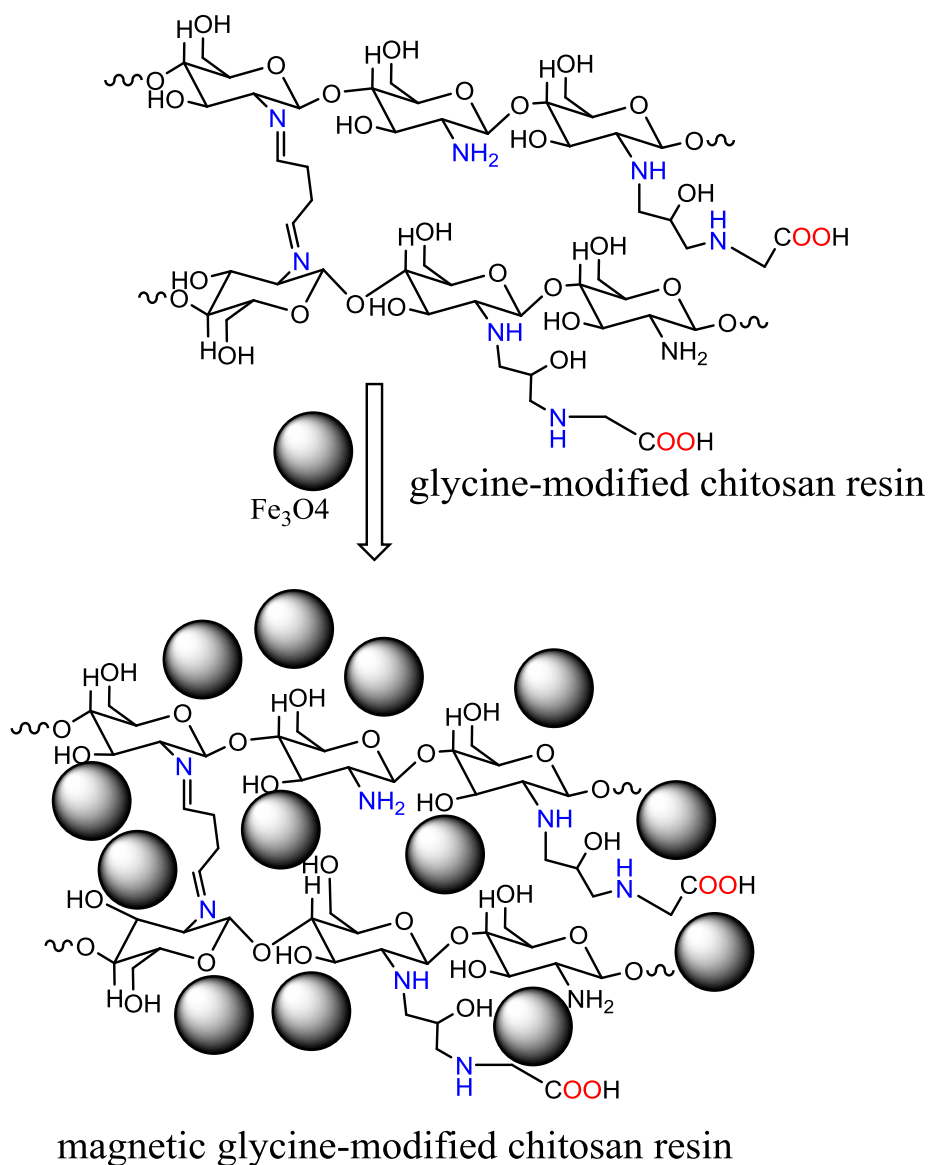
2.2.1 Preparation of magnetite

Magnetite was prepared using the following method (El Ghandoor *et al.*, 2012). A 250 mL (0.4 M) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution was added with stirring to a freshly prepared 250 mL (0.2 M) of Fe(II) solution. This mixture is added to the boiling solution of 500 NaOH (0.5 M) within 10 second under constant stirring. A black precipitate was formed and was allowed to crystallize for 30 min with stirring. The precipitate was washed with deoxygenated water (water was boiled to repeal any gases then bubbled with nitrogen gas) under magnetic decantation until the acidity of suspension became below pH 7.5. The precipitate was dried at room temperature to give a dry black powder.

2.2.2 Synthesis of magnetite chitosan

The glutaraldehyde-crosslinked chitosan glycine type was prepared as in literature (Khalil *et al.*, 2013). Briefly, three grams of chitosan was dissolved in 20% aqueous solution of acetic acid and stirred until the solution became homogenous. Then 1 mL of glutaraldehyde solution (50%) was added and the solution was stirred with heating for two hours. The pH of the solution was raised to 6 with 1M NaOH and the obtained gel was washed with distilled water several times and kept to dry. The cross-linked chitosan gel obtained in the previous step was suspended in 70 mL isopropyl alcohol. Then 7 mL epichlorohydrine (62.5 mmol) dissolved in 100 mL acetone/water mixture (1:1 v/v) was added. The above mixture was stirred for 24 h at 60 °C. The solid product obtained was filtered off and washed several times with water followed by ethanol. The product and

glycine (10 g) were suspended in dioxane (100 ml), then 40ml NaOH (1M) was added and the mixture was refluxed for 3 h. The final product was filtered and washed 3 times with ethanol and with deionized water. The obtained cross-linked chitosan gel from the previous step was suspended in water and the powdered Fe_3O_4 was added in 1:2 ratio (chitosan-gly : magnetite). The mixture was refluxed for 6 h on water bath at 75-80°C with continuous stirring. A grayish precipitate was formed, filtered off and washed with deionized water and kept to dry at 60 °C for 24h. The schematic structure of the magnetic glycine-modified chitosan resin is shown in Scheme 1.



Scheme 1 synthesis of magnetic glycine-modified chitosan resin (MGMCR)

2.3. Uptake experiments using batch method

2.3.1. Preparation of solutions

Stock solution (1000 ppm) of cadmium was prepared by dissolving 2.317g cadmium acetate dihydrate in 1L bi-distilled water. All batch experiments were carried out with adsorbent samples in a 250 mL conical flasks with 100 mL Cd (II) aqueous solutions on a rotary shaker at 200 rpm. The concentration of Cd(II) ions was determined using atomic absorption spectroscopy.

2.3.2. Effect of pH

The uptake of Cd (II) by MGMCR was studied at different pH values from 2 to 7. The pH was adjusted using HCl or NaOH. 0.1 g of investigated resin was placed in a series of flasks. To each flask 100 mL of Cd (II) solution (100 ppm) was added. The contents of each flask were shaken for 120 min on a shaker at 25 ± 1 °C and desired pH. The resin was separated from the solution by filtration. Then the residual concentration of Cd (II) was determined.

2.3.3 Effect of contact time

The effect of contact time is carried out by agitate the adsorption system in temperature controlled incubation shaker for different time intervals (20 to 180 min) at an optimum condition (initial metal ion concentration = 200 mg/l, solution pH = 5.0, MGMCR dose = 0.1 g, temperature = 25°C and volume of sample = 100 ml for Cd(II) ions solution. After the predetermined time interval, the concentration of the ions in the solution (supernatant) was analyzed by using atomic absorption spectroscopy (AAS). The amount of Cd(II) ion adsorbed onto MGMCR at different contact time was calculated by using the following equation:

$$qt = (C_0 - C_t)V/m \quad (1)$$

where qt is the amount of Cd(II) ion adsorbed onto MGMCR at any time t (mg/g), C_t is the final concentration of Cd(II) ion in the solution at time t (mg/l), V is the volume of Cd(II) ions solution (L), m is the mass of the MGMCR (g).

2.3.4. Adsorption isotherms

Complete adsorption isotherms were carried out by placing 0.1 g portions of dried resin in a series of flasks containing 100 mL of Cd (II) ions at pH 5.. The residual concentration of Cd (II) was determined. The percentage removal of Cd(II) ion from the solution can be calculated by using the following formula:

$$\% \text{ Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

3.1 Characterization of the adsorbent magnetic glycine-modified chitosan resin (MGMCR)

The XRD pattern of the final powders is shown in Figure 1. The XRD spectrum exhibited peaks corresponding to Fe_3O_4 , marked with their indices (220) at $2\theta = 32.5^\circ$, (311) at $2\theta = 35.4^\circ$, (400) at $2\theta = 43.4^\circ$, (422) at $2\theta = 53.9^\circ$, (511) at $2\theta = 57.2^\circ$ and (440) at $2\theta = 62.4^\circ$, which is similar to that reported before for Fe_3O_4 nanoparticles (El Ghandoor *et al.*, 2012; Liao and Chen, 2001) indicating that the Fe_3O_4 NPs are well crystalline.

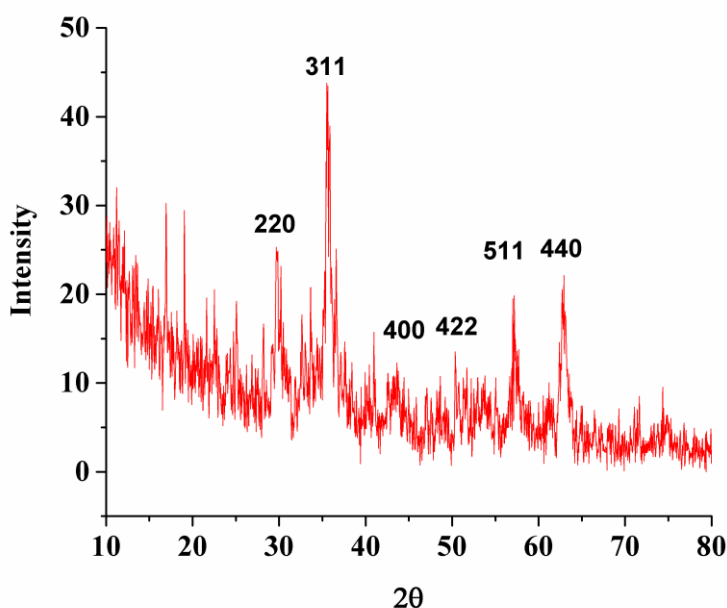


Fig. 1. The X-ray diffraction pattern of Fe_3O_4 nanoparticles in MGMCR Resin

TEM micrograph of the colloidal dispersions of MGMCR was obtained by a transmission electron microscope and the typical TEM micrograph for the chitosan-bound Fe_3O_4 nanoparticles is shown in Fig. 2. It is clear that the chitosan can inhibit the aggregation of nanoparticles because of the steric repulsion. So, chitosan-bound Fe_3O_4 nanoparticles had essentially mean diameter of about 25 nm as the nanoparticle size of non-bound Fe_3O_4 .

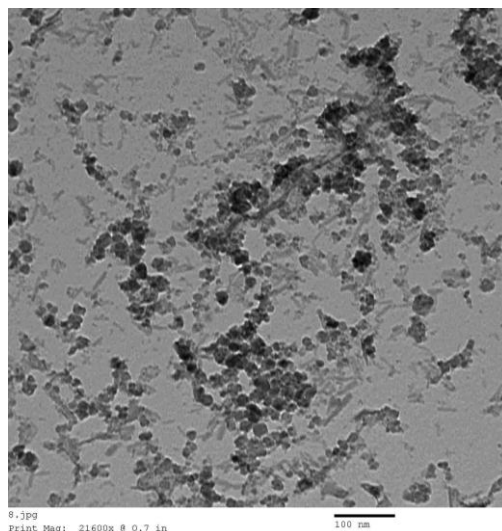


Fig. 2 TEM micrograph showing the size and distribution of Fe₃O₄ nanoparticles in MGMCR

FTIR

The FTIR spectra (400-4000 cm^{-1}) of the chitosan, glycine-modified chitosan and magnetic glycine-modified chitosan resin are shown in Figure 3. Usually, the major peaks of the chitosan, Fig. 3a, are located at 3420 cm^{-1} that attributed to O-H and N-H stretching vibrations and the peak at 2882.9 cm^{-1} due to -CH stretching vibration in -CH, and -CH₂ and the stretching vibration at 1650 cm^{-1} for NH stretching bending vibration. The band observed at 1320 cm^{-1} is assigned to C-N bending (Li and Bai, 2005). Also, the IR spectrum for chitosan has a sharp peak at 1420 cm^{-1} , which is caused by the presences of the primary amine group, NH₂. Meanwhile, based on the spectrum of glycine-modified chitosan beads, there is a significant new peak at 1659 cm^{-1} , which can be attributed to an imine bond (C=N), Fig. 3.b. The new bands at 1500 cm^{-1} and at 1424 cm^{-1} can be assigned to COO⁻ (stretching vibrations from glycine). The IR spectrum of magnetic crosslinked chitosan glycine exhibited bands similar to the glycine-modified chitosan with respective shift (Fig. 3c). Strong peak at 573 cm^{-1} (Fe-O vibration of Fe₃O₄) indicated presence of Fe₃O₄ nanoparticles in MGMCC material (Yuwei and Jianlong, 2011).

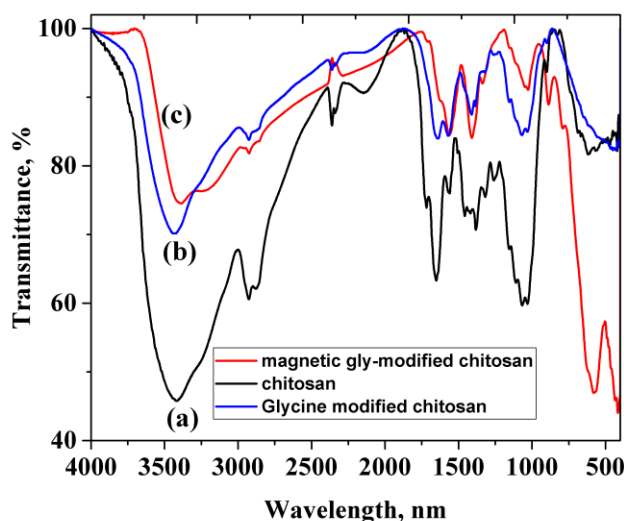


Fig. 3. FTIR spectra of (a) chitosan (b) glycine modified chitosan, and (c) magnetic modified chitosan-bound Fe_3O_4 nanoparticles.

Thermal Analysis

The overall thermogravimetric decomposition process of chitosan, glycine modified chitosan derivative and its magnetic modified chitosan-bound Fe_3O_4 nanoparticles under nitrogen is presented in Fig. 4. TG curve of chitosan is a smooth curve with only two weight-loss steps, which are well explained in the literature (**Mucha and Pawlak, 2005; Ziegler-Borowska *et al.* 2016**). The first step, occurring at lower temperatures (20–120 $^{\circ}\text{C}$), is assigned to releasing of adsorbed water, which is obvious because of the CS hydrophilicity. The main destruction of chitosan biopolymer takes place in the second stage in the temperature range of 200–500 $^{\circ}\text{C}$ indicating that the thermal degradation of chitosan in nitrogen atmosphere is simple and is a one-step reaction after dehydration. It was repeatedly confirmed that the main chain split, abstraction of side groups and ring opening reactions occur in this step. The carbonaceous residue in N_2 atmosphere is about 35 % at 800 $^{\circ}\text{C}$ (but even at 1000 $^{\circ}\text{C}$ the decay is not completed).

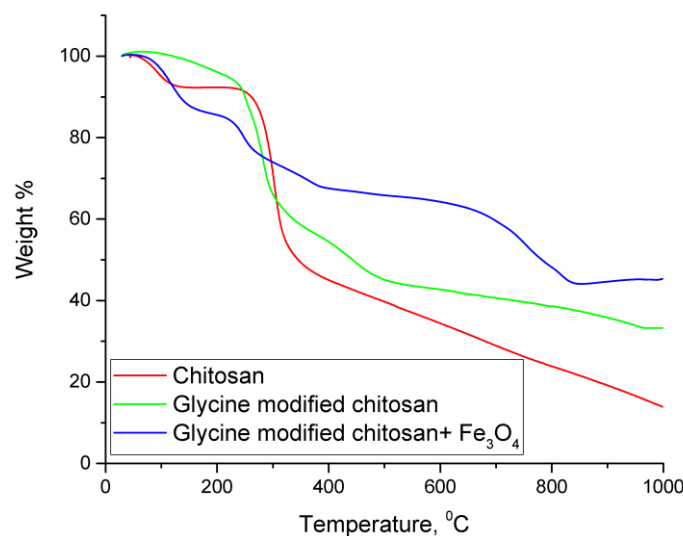


Fig. 4. Thermogravimetric curves of chitosan, glycine modified chitosan and magnetic glycine modified chitosan.

Thermogravimetric curves of modified chitosan exhibit three steps in the studied temperature range. The first two steps are overlapped and start at room temperature and proceeds to about 368 °C, represent about 40% due to decomposition of chitosan and the second step extends to around 495 °C with weight loss of 13.16%. Finally, at higher temperatures (> 500 °C) the decomposition is continued and systematic mass loss without any maximum rate is observed giving residue of 35%.. Thermogravimetric profiles of MGMCR vary from the chitosan and chitosan derivative. TG curves of MGMCR with Fe₃O₄ (Fig. 4) show four steps of thermal degradation. The first step starts at from 32 to 187 °C with weight loss of 14.2% due to water desorption. The other three steps continue degradation with remaining weight percent of 44.29% which is higher than chitosan or modified chitosan. The meaningful difference is caused by high residue at the end of experiment due to the inorganic part presence. The last step of MGMCR thermal decomposition, occurring above 600 °C, can be assigned to changes in the inorganic core.

Investigation of the removal ability of the magnetite glycine modified chitosan resin in aqueous media

Removal study of cadmium using magnetite glycine modified chitosan bound Fe₃O₄ nanoparticles MGMCR is carried out at optimal experimental conditions. Then, first, the removal efficiency was optimized by changing the experimental factors one at a time.

Effect of pH

The adsorption of the solutions containing Cd(II) ions (100 ppm) by the chitosan-bound Fe₃O₄ nanoparticles (as a magnetic nano-adsorbent) was investigated in aqueous solutions for pH range 2–7, Fig. 5, at room temperature. The removal efficiency of Cd(II)

increased with increasing pH to a maximum value at pH 5 and then declined. This can be explained with the fact that, in the strong acid solution more protons will be more available to protonate the nitrogen of chitosan and amino acid groups reducing the binding sites for Cd(II) ions. With the increase of pH, the amino groups become free from protonation due to a decrease in the concentration of hydrogen ions leading to the decrease in competition of H^+ with metal ions for sorption sites and thus the adsorption capacity increases. Cd^{2+} ions, which is the main hydrolyzed cadmium species in the pH range 5.0–7.0 appears in the form of $Cd(OH)^+$, $Cd(OH)_2$, and $Cd(OH)_3^-$. The fraction of negatively charged hydrolysis products in the solution increases as pH increases (Madala *et al.*, 2017). Therefore, pH 5 was selected as optimum condition for adsorption of Cd(II) on MC

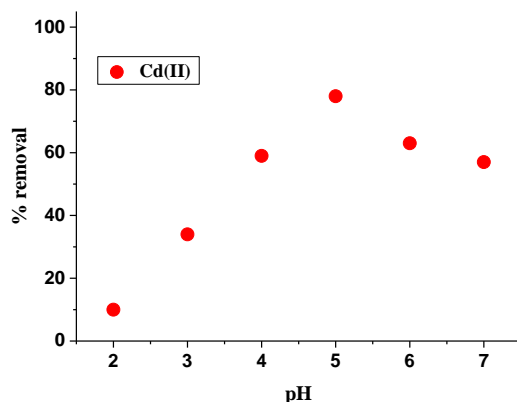


Fig. 5. Effect of pH on percent removal of Cd(II) onto MGMCC. (Experimental conditions: initial conc. 100 mg/L, contact time 2 h, adsorbent dose 0.1g, time:120 min, 200 rpm and temperature 25 °C).

3.3. Effect of adsorbent dosage

The experiments on the effect of amount of adsorbent on adsorption of Cd(II) were performed at pH 5.0 with 100 ml of adsorbate solution by varying the amount of adsorbent from 0.05 to 0.2 g. The percent removal of Cd(II) ions increases with increase of amount of MGMCC due to the greater availability of active binding sites of the modified chitosan. The maximum removal efficiency is with 0.1 g of MGMCC and the maximum percent removal is about 82% (Fig. 6).

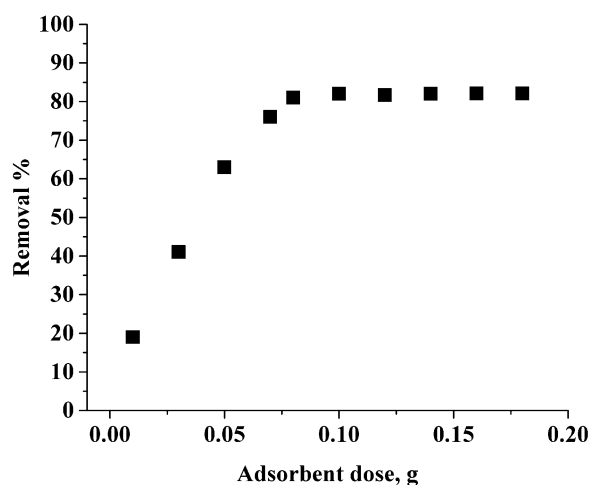


Fig. 6. Effect of adsorbent dose on percent removal of Cd(II) onto MGMCC. (Experimental conditions: initial conc. 100 mg/L, contact time 2 h, pH 5.0, 150 rpm).

3.4 Adsorption kinetics

The effect of contact time on the removal of Cd (II) ions by the MGMCC has been investigated over the range from 10 to 180 min with initial concentrations of 50, and the results are shown in Figure 7. The contact time curves show rapid adsorption rate of Cd (II) ions is increased. After that, uptake rate slowly declines with lapse of time and tends to be equilibrium at 2 h. It can be explained that there were plenty of available adsorption sites. With the adsorption process proceeding, the adsorption sites were occupied gradually and the percent removal elevated slowly and the adsorption reaches its equilibrium in 2 h. Therefore, the optimum contact time for adsorption of Cd(II) is about 120 min.

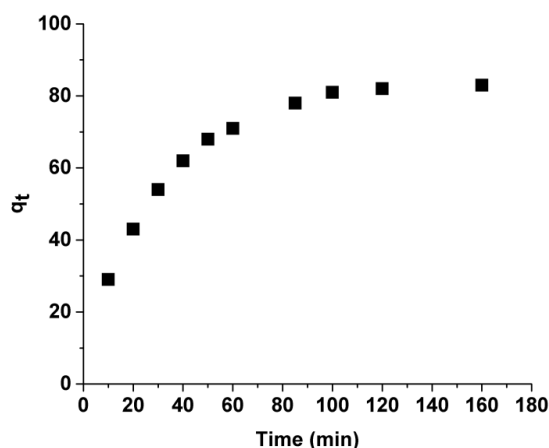


Fig. 7. Effect of contact time on adsorption of Cd(II) (initial concentration 200 mg L⁻¹, MGMCC, 2 g/ L, pH 5.0, shaking rate 150 rpm, 30 °C).

3.5 Adsorption isotherm

Adsorption isotherm studies are performed to reflect the performance of adsorbents in adsorption processes. Many isotherms are well-known (Wang and Guo, 2020) and in this study, Langmuir and Freundlich are used to determine the adsorption equilibrium between the adsorbent and the metal ion. The Langmuir isotherm model assumes that a monomolecular layer is formed when adsorption takes place without any interaction between the adsorbed molecules. The Langmuir model can be represented as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \quad (3)$$

where q_e the adsorbed value of Cd(II) ions at equilibrium concentration (mg/g), Q_{\max} is the maximum adsorption capacity (mg/g) and K_L is the Langmuir binding constant which is related to the energy of adsorption ($L \text{ mg}^{-1}$), C_e is the equilibrium concentration of Cd(II) in solution (mg/L).

The experimental data were plotted as C_e/q_e versus C_e in order to evaluate the values of Langmuir constants q_m and K_L . The important characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by

$$R_L = \frac{1}{1 + K_L C_i} \quad (4)$$

where C_i (mg g^{-1}) is the highest initial concentration of adsorbate and R_L values $0 < R_L < 1$ imply favorable adsorption, unfavourable when $R_L > 1$, and irreversible when $R_L = 0$.

The Freundlich isotherm model is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the concentration of metal ion at equilibrium. This isotherm model is defined by the equation (Ayawei *et al.*, 2017) below:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where The values of K and $1/n$, which roughly correspond to the adsorption capacity and the heterogeneity factor, respectively.

Isotherm parameters for the Langmuir and Freundlich models for the (GMCCR) are presented in Table 1. At 25°C the maximum uptakes for (GMCCR) are 172 mg/g. . The values of K_L and Q_{\max} for adsorption of Cd (II) on resin was calculated from Langmuir isotherm (Fig. 7b). The values of R^2 reported in Table 1, which is a measure of the goodness-of-fit, confirm the better representation of the experimental data by Langmuir model. This indicates the homogeneity of active sites on the resin surface and suggest that the adsorption of Cd(II) occurred mainly by monolayer reaction.

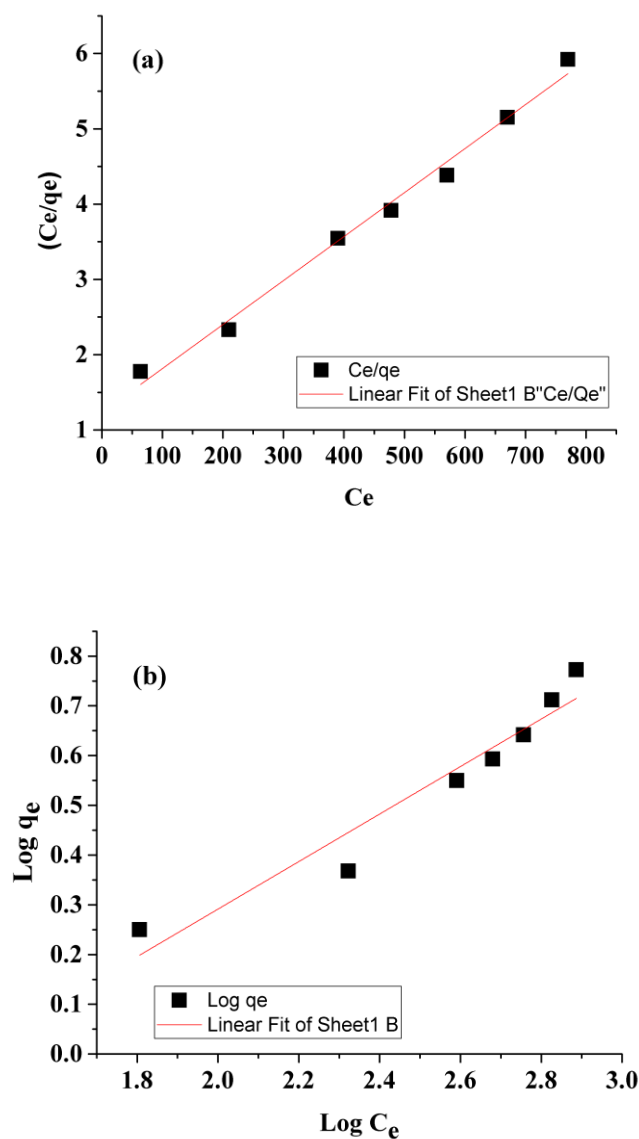


Fig. 8. (a) Langmuir and (b) Freundlich isotherms for the adsorption of Cd(II) on (MGMCR) at room temperature; pH 5; contact time 120 min.

Table 1 Isotherms constants for adsorption of Cd (II) on magnetic Chitosan-Glycine resin

Temp. (K)	Langmuir constants			Freundlich constants		
	$Q_{\max},$ (mg/g)	K_L (L mg ⁻¹)	R^2	$1/n$	K_f	R^2
298	172.41	0.1912	0.990	0.4778	0.216	0.933

CONCLUSION

The present study showed that the magnetic modified chitosan prepared with simple preparation method and low cost is a promising green biosorbent that is expected to be applied effectively in treatment of the wastewater effluents from cadmium industry in the future..

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