

ORIGINAL RESEARCH PAPER

Application of Sulfur-Modified Magnetic Nanoparticles for Cadmium Removal from Aqueous Solutions

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ABSTRACT

Even at low levels, heavy metals are toxic and can damage living things. They do not break down or decompose and tend to build up in plants, animals, and people causing health concerns. Magnetic nanoparticles (MNPs) can be considered as potential adsorbents for the removal of cadmium (Cd^{2+}) from aqueous solutions because of their high surface area and the combined effect of adsorption and separation under external magnetic fields. In this study, a novel sulfur-modified magnetic nanoparticle was applied as an adsorbent for the removal of Cd^{2+} ions from aqueous solutions. The adsorbent was characterized by scanning electron microscopy (SEM), Fourier transform-infrared (FT-IR) spectroscopy, and thermogravimetric analysis (TGA). The effects of pH, contact time, and initial concentration of Cd^{2+} on the removal efficiency of it were investigated in batch adsorption experiments. The equilibrium data fitted the Langmuir isotherm model better than the Freundlich isotherm model, and they were well explained in terms of pseudo-second-order kinetics. The maximum monolayer capacity q_m and K_L the Langmuir constant were calculated from the Langmuir as 5.1867 mg/g and 0.1562 L/mg, respectively.

Keywords: Adsorption, Cadmium, Magnetic Nanoparticles (MNPs), Removal

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INTRODUCTION

Heavy metals are metallic elements with high atomic weights, such as mercury, chromium, cadmium, arsenic, lead, etc. Even at low levels these metals are toxic and can damage living things. They do not break down or decompose and tend to build up in plants, animals, and people causing health concerns [1, 2]. Depending on the metal, its concentration, route of exposure, as well as the age, genetics, and nutritional status of exposed targets, heavy metals can have a variety of environmental and health concerns [2, 3].

Cadmium (Cd^{2+}) is extensively applied in

batteries (nickel-cadmium batteries), pigments, alloys, phosphate fertilizers and metal plating [4-6]. Galvanized pipes, discharge from metal refineries, the ash combustion of fossil fuels, runoff from waste batteries and paints can be the major sources of exposure of Cd^{2+} in water [6, 7]. Kidney damage, stomach problem, diarrhoea and sometimes death are adverse health effects that have been observed in human beings by ingestion of Cd^{2+} . Accumulation of Cd^{2+} in body impacts different organs such as liver, lungs, intestines, placenta, and pancreas [6, 8-9]. High exposure of human populations to Cd^{2+} and excessive intake of Cd^{2+} causes serious illnesses

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such as itai-itai disease [6, 10] and impacts the reproductive hormone levels [6, 8, 11]. Maximum contamination levels (MCLs) for Cd²⁺ in air, sludge (soil), drinking water and supporting aquatic life regulated by United States Environmental Protection Agency (U.S. EPA) are 0.1-0.2 (mg/m³), 85 (mg/kg), 0.005 (mg/L) and 0.008 (mg/l), respectively [2, 12]. The permissible Cd²⁺ concentration as per World Health Organization (WHO) guidelines in drinking water is 0.003 mg/L [6, 7]. Thus, it is essential to take considerable effort for developing effective treatment techniques for removal of Cd²⁺ ions from wastewater before its discharge into the near water bodies [13].

Precipitation, floatation, ion exchange, membrane processes (e.g. ultrafiltration, reverse osmosis), solvent extraction, coagulation, flocculation, electro dialysis, electrochemical reduction, phytoextraction, biological processes, ionization, and adsorption are various techniques which have been applied for the removal of Cd²⁺ from aqueous solutions. Most of them have their own drawbacks because of high operating cost, sludge generation and laborious techniques [13, 14]. Among these applied techniques, adsorption can be considered most effective and suitable for Cd²⁺ removal [13, 15]. In real, adsorption can be usually considered as one of the most frequently applied and promising technologies due to its low cost, easy operation, high efficiency, the simplicity of the equipment and easy regeneration [6, 14, 16, 17]. Since the performance of an adsorptive separation is directly rely on the quality and cost-effectiveness of the adsorbent, in the recent years, there has been a continuous interest in the development of effective noble adsorbents with high surface areas and more binding sites [14, 18].

Magnetic nanoparticles (MNPs) can be considered as potential adsorbents for the removal of Cd²⁺ from aqueous solutions because of their high surface area and the combined effect of adsorption and separation under external magnetic fields. Because iron-based materials are inexpensive and environmentally friendly, therefore, they can be mostly interesting [6, 19, 20]. These iron-based nanomaterials can be synthesized by microwave assisted irradiation of iron, pulsed current and chemical methods [6, 20-23]. Due to the importance and very wide utilization of MNPs, some researchers recently reviewed their synthesis methods and applications in several scientific fields [6, 24-26].

MNPs have widely been applied as new adsorbents with a large surface area for the

separation and removal of metals such as Cd²⁺ from aqueous solutions. Huang *et al.* applied γ -mercaptopropyltrimethoxysilane (γ -MPTMS)-modified silica-coated MNPs as solid phase extraction (SPE) adsorbent for separating and concentrating trace amounts of Cd, Cu, Hg, and Pb before analysis by inductively coupled plasma-mass spectrometry (ICP-MS). The modified nanoparticles are highly monodisperse, magnetically separable, and provide high adsorptive capacities; they can rapidly and quantitatively adsorb Cd, Cu, Hg, and Pb from 250 mL aqueous solution in 10 min [24, 27]. Faraji *et al.* investigated the application of decanoic acid coated Fe₃O₄ nanoparticles as an adsorbent for solid phase extraction and determination of trace amounts of Cd, Co, Cr, Ni, Pb and Zn from environmental water samples using flow injection inductively coupled plasma-optical emission spectrometry (ICP-OES). Under the optimized conditions, detection limits for Cd, Co, Cr, Ni, Pb, and Zn were reported to be 0.3, 0.7, 0.5, 0.6, 0.8 and 0.2 μ g/L, respectively [23]. Gupta and Nayak modified an agricultural waste-orange peel powder (OPP) into a novel magnetic nano-adsorbent (MNP-OPP) by coprecipitating it with Fe₃O₄ nanoparticles (MNP) for Cd²⁺ ion removal from aqueous solutions. Results demonstrated a faster kinetics and efficiency of MNP-OPP in comparison to those of MNP and OPP and further confirmed a complexation and ion exchange mechanism to be operative in metal binding. Cd²⁺ removal was achieved at 82% from a simulated electroplating industry wastewater [18]. Singh *et al.* synthesized citric acid coated magnetite nanoparticles (Fe₃O₄-Cit) for the removal of Cd²⁺ from aqueous solutions and reported that the experimental data could be suitable linearity with Langmuir isotherm having maximum adsorption capacity (q_m) values in mg/g 10.81, 11.45 and 12.56 at the 298 K, 303K and 308 K, respectively [13]. Shan *et al.* studied the adsorption kinetic, isothermal, thermodynamic and mechanistic properties of Cd²⁺ in an aqueous solution containing Mg-Al-CO₃- and magnetic Fe₃O₄/Mg-Al-CO₃-layered double hydroxide (LDH) and reported that the adsorption kinetics and isotherm data followed the pseudo-second-order model and the Langmuir equation, respectively. The adsorption process of Cd²⁺ reported being feasible, spontaneous and endothermic in nature [14]. Huang *et al.* synthesized magnetic nanoparticle adsorbents, namely Mag-PCMA-T, which contain a maghemite

core and a silica mesoporous layer that permanently confines surfactant micelles within the mesopores, to achieve simultaneous removal of polycyclic aromatic hydrocarbons (PAHs) (1 mg/L) and metal contaminants (1 mg/L). They reported that Mag-PCMA-T removed >85% of the acenaphthene in <30 min, with relatively high sorption capacity (up to 1060 mg/kg). Mag-PCMA-T also exhibited high sorption capacity for Cd²⁺ (up to 2250 mg/kg). The simultaneous sorption performance was stable across a wide pH range (4–9) as well as in the presence of competitive metal ions (Cd²⁺ and Mg²⁺) or natural organic matters [28]. Chen *et al.* prepared a novel composite of carbon disulfide-modified magnetic ion-imprinted chitosan-Fe(III), i.e., MMIC-Fe(III) composite, as an efficient adsorbent for the simultaneous removal of tetracycline (TC) and Cd²⁺. They mentioned that the adsorption proceeded according to a pseudo-second-order model and the adsorption isotherms were well described by the Langmuir model, with maximum adsorption capacity for TC and Cd²⁺ being 516.29 and 194.31 mg/g, respectively. They concluded that the synergistic effect of TC and Cd²⁺ adsorption might be due to the formation of TC- Cd²⁺ complex bridging the adsorbate and adsorbent [29].

Li *et al.* [30] studied a novel magnetic polydopamine (PDA)-LDH (MPL) bifunctional material, that was synthesized by an easy and green method for the simultaneous removal of potentially toxic metals and anionic dyes and concluded that the MPL assemblies had practical utilization potential for integrative and efficient treatment of coexisting toxic pollutants [30]. Beyki *et al.* [31] investigated the green synthesis of Fe₃O₄ nanoparticles as a magnetic core to prepare poly 1, 4 phenylenediamine nanocomposite and used this magnetic polymer nanocomposite as an adsorbent in the removal of Pb²⁺ ions and Direct red 81 (DR-81) from single and binary solutions. The maximum capacity of this nanocomposite was reported to be 144.92 and 370.37 mg/g for DR-81 and Pb²⁺, respectively [31].

In this study, a novel sulfur-modified magnetic nanoparticle was synthesized as an adsorbent for the removal of Cd²⁺ ions from aqueous solutions. The novel adsorbent was characterized by scanning electron microscopy (SEM), Fourier transform-infrared (FT-IR) spectroscopy, and thermogravimetric analysis (TGA). The batch adsorption study was performed on the synthesized adsorbent to investigate the effect of pH, contact

time, and initial concentration of Cd²⁺ on the removal efficiency and the adsorption capacity for cadmium uptake. Also, the kinetics and adsorption isotherms were investigated.

MATERIAL AND METHODS

Materials and reagents

All chemicals and reagents used were of analytical grade without any further purification. Isopropylamine ((CH₃)₂CHNH₂), carbon disulfide (CS₂), 3-(Chloropropyl)-trimethoxysilane (Cl(CH₂)₃Si(OCH₃)₃), cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O), toluene (C₆H₅CH₃), methanol (CH₃OH), ethanol (C₂H₅OH), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from the Merck (Darmstadt, Germany). Fe₃O₄ nanoparticles were of laboratory grade and were prepared by a chemical co-precipitation method [32]. Double-distilled deionized water was applied to preparing solutions.

Preparation of the adsorbent

For the preparation of new adsorbent, the magnetic Fe₃O₄ nanoparticles firstly functionalized by 3-(Chloropropyl)-trimethoxysilane. Briefly, 10.0 g of Fe₃O₄ nanoparticles were mixed with 6.5 mL of 3-(Chloropropyl)-trimethoxysilane and 50.0 mL of toluene. After 24 h, the mixture was filtered and washed three times with 20.0 mL toluene and two times with 20 mL ethanol; afterward, it was dried at vacuum oven under conditions of 50 °C for 12 h (Fig. 1A). Next step is a sulfur modification of the mixture. In real, the sulfur groups have a strong affinity binding for most heavy metals [29]. For this purpose, 5.0 mL carbon disulfide was slowly added to 1.64 mL isopropylamine under mild heat condition to form a white precipitated (Fig. 1B). Then, 0.54 g of this sulfur compound was dissolved in 10.0 mL methanol and afterward 0.2 g of the magnetic Fe₃O₄ nanoparticles functionalized by 3-(Chloropropyl)-trimethoxysilane were added to it and kept at 65.0 °C for 24 h (condenser condition). The final products were obtained after filtering and drying at 50.0 °C in a vacuum oven for one hour (Fig. 1C) and are hereafter referred as sulfur-modified magnetic nanoparticles (SM-MNPs). The chemical structure of synthesized novel adsorbent is shown in Fig. 2.

Characterization of the adsorbent

The morphology and surface structure of the adsorbents were studied using scanning electron

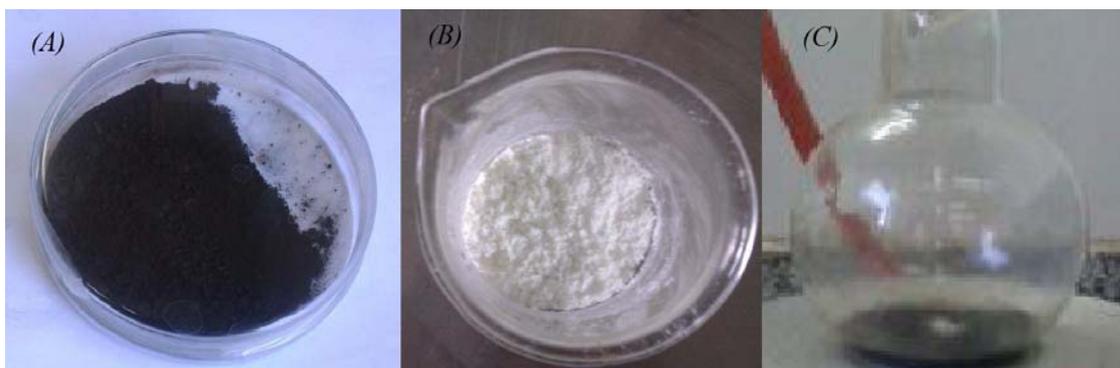


Fig. 1. Novel adsorbent synthesis steps: (A) the magnetic Fe_3O_4 nanoparticles functionalized by 3-(Chloropropyl)-trimethoxysilane, (B) the product of reaction of carbon disulfide and isopropylamine, and (C) the synthesized final adsorbent.

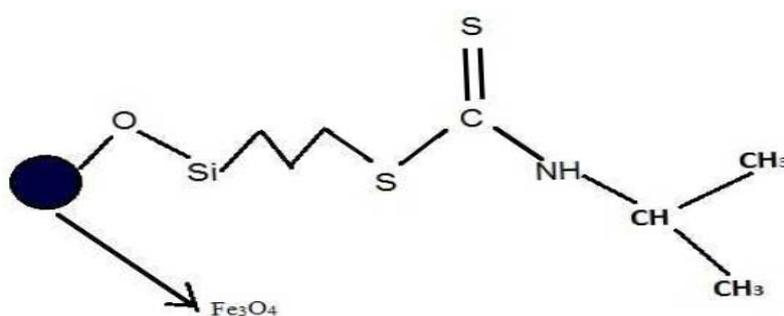


Fig. 2. The chemical structure of the synthesized novel adsorbent.

microscopy (SEM) (Model S-360, Cambridge Instruments Ltd.). The surface functional groups of samples were determined by Fourier transform-infrared (FT-IR) (Bruker Vector 33 FT-IR, Germany). Thermal stability of MNPs was studied by a Rheometric Scientific STA 1500 thermogravimetric analysis (TGA) instrument at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ in the temperature range of $25\text{--}700\text{ }^\circ\text{C}$ under nitrogen atmosphere.

Adsorption procedure

The cadmium stock solution was prepared by dissolving cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) in distilled water and then diluting with distilled water to a specific concentration. Adsorption processes for all experiments were conducted in a 15 mL falcon tube containing 0.05 g of the adsorbent and 15 mL of cadmium solution with certain concentration and pH, which was shaken at room temperature for a given time. The pH of the cadmium solution was adjusted to the appropriate value with 0.1 mol/L HCl and NaOH. After adsorption, the suspensions of the adsorbent and Cd^{2+} in an aqueous solution were separated using a permanent magnet. The

residual Cd^{2+} concentrations in the supernatant clear solutions were determined by Varian atomic absorption spectrometer using a calibration curve (accuracy and precision with $< 2\%$ error). In real, the effects of the pH, contact time, and initial concentration of cadmium on removal efficiency were studied. The effect of pH on the sorption of the adsorbent toward Cd^{2+} was determined by mixing 0.05 g adsorbent with 15 mL of a solution containing Cd^{2+} (1 mg/L) at various initial pH levels (2, 3, 4, 5, and 6).

Then, the kinetics and adsorption isotherms were investigated. For the kinetics study experiment, 0.05 g of the adsorbent was added to 15 mL of a solution with the initial concentrations of Cd^{2+} adjusted to 1 mg/L. The mixture was shaken. Samples were withdrawn at different time intervals (5, 10, 20, 30, 40 and 60) and analyzed for the residual concentrations. The adsorption isotherm study was established for the adsorbent (0.05 g) in the 15 mL of cadmium solution with different initial concentrations of Cd^{2+} (5, 10, 20, 30, 40, and 50 mg/L) at optimal contact time. The pH of the solution in kinetics and sorption isotherm studies were adjusted to the optimal pH obtained in the

pH effects study. Other procedures were the same as those described in the experiment on pH effect. All the adsorption experiments were carried out at ambient temperature (22-25 °C).

The removal efficiency (E) and the adsorption capacity for cadmium uptake, q_e (mg/g), were determined as follows:

$$E(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C) \times V}{m} \quad (2)$$

where C_0 (mg/L) is the initial concentration of Cd^{2+} , C (mg/L) denotes the final concentrations of Cd^{2+} , m (g) is the mass of adsorbent, and V (L) denotes the volume of adsorbate (Cd^{2+}) solution.

Adsorption model fitting

The equilibrium adsorption of Cd^{2+} ion was evaluated according to Langmuir and Freundlich isotherms by Eqs. (3) and (4), respectively [28, 33]:

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

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

where C_e is Cd^{2+} concentration (mg/L) at equilibrium and q_e is amount adsorbed (mg/g), q_m is the maximum sorption capacity (mg/g), K_L (L/mg) and K_F (mg/g)/(L/mg)⁻ⁿ are the Langmuir and Freundlich sorption equilibrium constants, respectively. The Langmuir model is suitable for monolayer adsorption on a surface, whereas, Freundlich model is used on the basis of premising

that stronger binding sites are occupied first [16].

Kinetics were analyzed using the pseudo-second-order model as presented in Eq.(5) [13, 14, 28, 31]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_t and q_e (mg/g) are the amounts adsorbed at time t (min) and equilibrium, respectively, and k [g/(mg.min)] is the rate constant of pseudo-second-order model.

RESULT AND DISCUSSION

Characterization of the adsorbent

SEM micrograph of the adsorbent depicts the morphological characteristics favorable for metal adsorption. Fig. 3 shows a spherical morphology of the adsorbent (slightly agglomerated) with a mean particle size of 100 nm.

The functional groups and surface properties of the adsorbent were confirmed by the FT-IR spectra. Fig. 4 shows FT-IR spectra of (A) the magnetic Fe_3O_4 nanoparticles functionalized by 3-(Chloropropyl)-trimethoxysilane, (B) the product of the reaction of carbon disulfide and isopropylamine, and (C) the synthesized final adsorbent. In the FT-IR spectrum of the magnetic Fe_3O_4 nanoparticles functionalized by 3-(Chloropropyl)-trimethoxysilane (Fig. 4A), the bond at 1399 cm^{-1} is related to C-Cl asymmetric stretching vibrations, and the peaks observed at 3045 , 3143 , 2807 , 593 , 1055 , and 1623 cm^{-1} could be assigned to the Si-O-H, asymmetric stretching vibrations of the C-H, Si-O, Si-O-Si vibrations, and O-H bending vibrations, respectively. In the FT-IR spectrum of the product of the reaction of carbon disulfide and isopropylamine (Fig. 4B), the

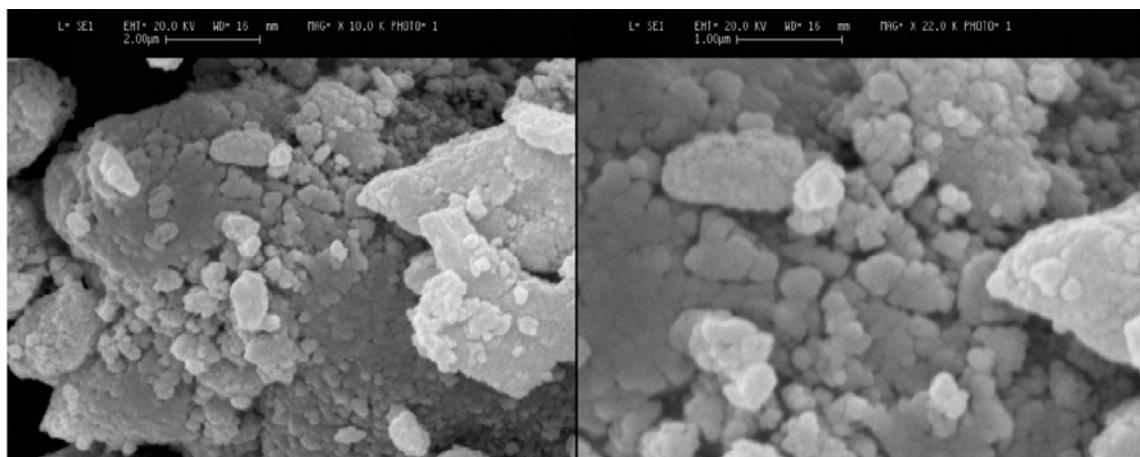


Fig. 3. SEM image of the adsorbent.

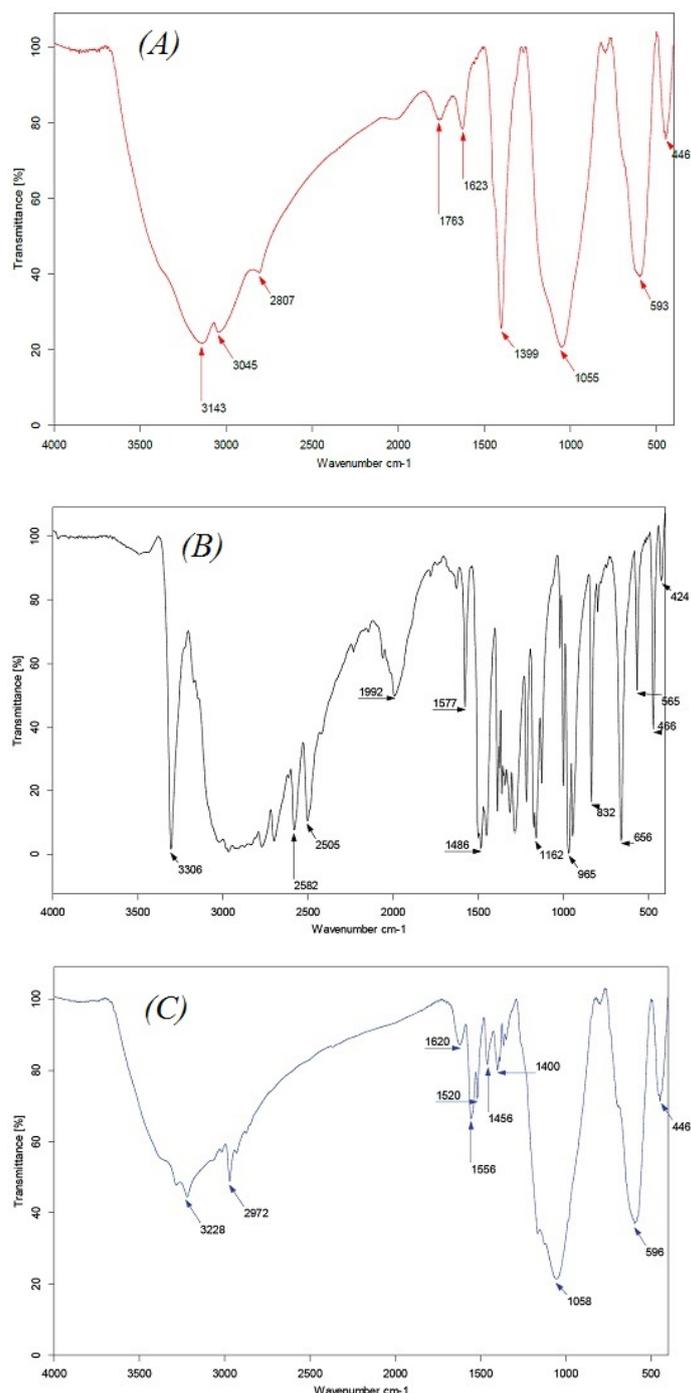


Fig. 4. FT-IR spectra of (A) the magnetic Fe₃O₄ nanoparticles functionalized by 3-(Chloropropyl)-trimethoxysilane, (B) the product of reaction of carbon disulfide and isopropylamine, and (C) the synthesized final adsorbent.

bonds at 1486 and 2582 cm⁻¹ are related to C-N and S-H vibrations, respectively, and the peaks at 3305 and 1162 cm⁻¹ could be assigned to the N-H deformation vibrations. In the FT-IR spectrum of the synthesized final adsorbent (Fig. 4C), the peaks observed at 2972, 1556, and 596 cm⁻¹ could

be assigned to the asymmetric stretching vibrations of the C-H, C-N, and Si-O vibrations, respectively. Also, C-Cl vibrations were disappeared on the synthesized final adsorbent. This may be evidence that the adsorbent was successfully modified and functionalized.

Fig. 5 show TGA graph of the adsorbent. TGA curve of the adsorbent depicts that the weight loss over the temperature 25 to 200 °C is about 6%. This might be because of the loss of residual water (physical and chemical water) in the sample. Then the principal chains of polymer begin to decompose at about 200 °C and the final temperature of degradation is around 300 °C. Here, the weight loss is 40%. At higher temperature (300 to 600°C), there is no significant change of weight. This implies that there are only Fe₃O₄ nanoparticles at this range of temperature and the presence of functional groups in/on the adsorbent are confirmed by TGA. This result is compatible with those of the other researches [28, 34].

Effect of operating conditions on the adsorption of Cd²⁺

The operating parameters such as initial solution pH, contact time, metal ion concentration and other parameters can affect the surface characteristics of the adsorbent surface and its metal binding capacity [18]. Thus, a batch adsorption study was performed on the synthesized adsorbent to investigate the effect of these operating parameters on the removal efficiency and the adsorption capacity for cadmium uptake.

Effect of pH

Fig. 6 shows the initial solution pH dependency of Cd²⁺ ion removal from aqueous solutions by the adsorbent. The adsorption capacity was low at lower pH values (for example 60.0% at pH=3). It seems that

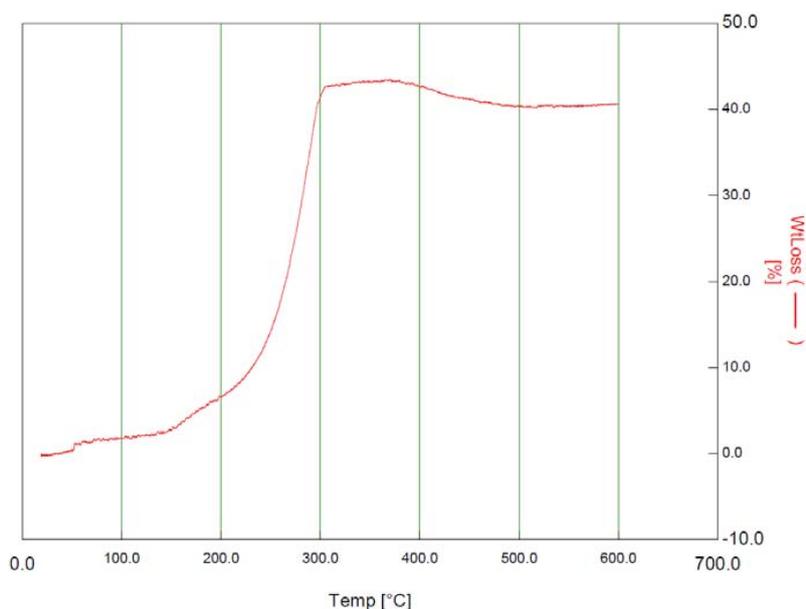


Fig. 5. Thermogravimetric analysis (TGA) of the adsorbent.

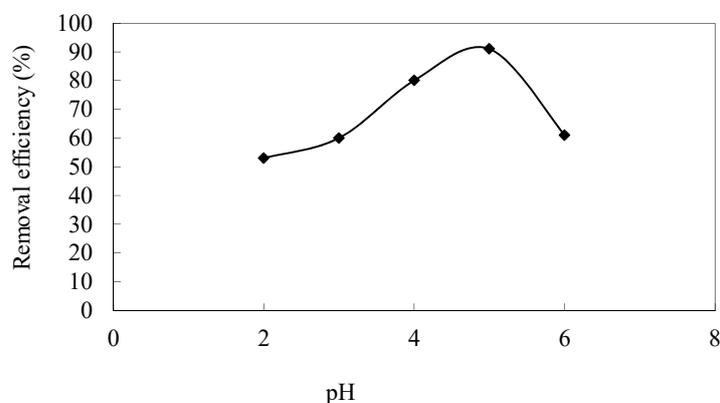


Fig. 6. The effect of initial solution pH on the removal efficiency of Cd²⁺ by the adsorbent.

the positive charge on the adsorbent is generated in the acidic pH (low pH). So, there is an electrostatic repulsion between the adsorbent and Cd^{2+} ions in solution. The hydrogen ions instead of cadmium ions are placed into the adsorbent sites when the amount of hydrogen ions increases in solution, and so the removal efficiency is low [35]. The removal efficiency of Cd^{2+} was increased with increasing pH from 60.0% to 92.0% in the pH range of 3–5 and then appeared to decrease at higher pH values. Therefore, the optimum pH was 5 for the removal of Cd^{2+} from the aqueous solution. The increase in the Cd^{2+} adsorption on the adsorbent with increasing pH may be attributed to the surface charge and the availability of binding sites presented at the adsorbent surface [14, 36, 37]. The obtained results of the present study are in line with the previous research findings [18, 35] and this pH strong dependency of the Cd^{2+} adsorption on the adsorbent was seen in Zhao *et al.* work [37].

Effect of contact time

Fig. 7. shows the effect of contact time on the removal efficiency of Cd^{2+} by the adsorbent. The

study of the removal efficiency of Cd^{2+} by the adsorbent revealed that the adsorption capacity of it enhanced with contact time up to 10 min and after that, the removal efficiency was approximately constant. For this reason, the optimum contact time was selected as 10 min. According to Fig. 7, with increasing contact time, Cd^{2+} ion removal efficiency increases, because Cd^{2+} ions have more opportunities for contact with the adsorbent surface when time enhances. The rate of Cd^{2+} ions removal was fast in the beginning times (first 10 min) due to the larger surface area of the adsorbent available [35]. As time increases to 60 min, there are no big changes in removal efficiency (very slightly decrease) due to the saturation of binding sites presented at the adsorbent surface.

Effect of initial concentration of Cd^{2+}

The effect of initial Cd^{2+} concentration on the removal efficiency of Cd^{2+} by the adsorbent is shown in Fig. 8. According to Fig. 8, with increasing Cd^{2+} concentration of 5–30 mg/L, the removal efficiency is increased from 70 to 86 %; and then appeared to

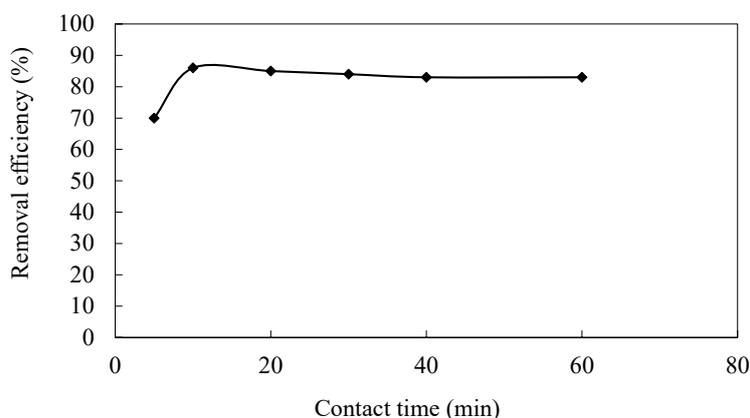


Fig. 7. The effect of contact time on the removal efficiency of Cd^{2+} by the adsorbent.

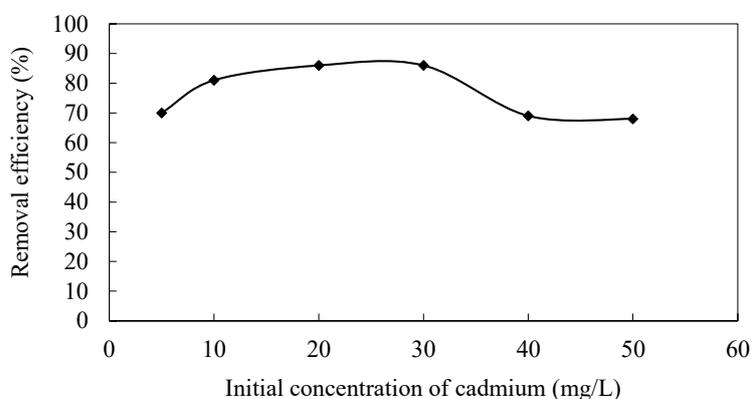


Fig. 8. The effect of initial Cd^{2+} concentration on the removal efficiency of Cd^{2+} by the adsorbent.

decrease at higher initial Cd^{2+} concentration values.

An enhanced ratio of an initial number of Cd^{2+} ions to the available surface area resulted in high concentration; hence fractional adsorption relies on initial concentration. For a given amount of the adsorbent (0.05 g of the adsorbent) the total number of available adsorption active sites is constant thereby adsorbing almost the same amount of Cd^{2+} , therefore, a decrease in the removal of Cd^{2+} resulted in an increase in initial concentration of Cd^{2+} due to the saturation of binding sites presented at the adsorbent surface [35, 38].

Adsorption isotherms

Equilibrium isotherms are applied to describe the experimental adsorption data. The parameters obtained from the different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent [32].

The Langmuir and Freundlich models were used to determine the adsorption isotherm for Cd^{2+} removal by synthesized adsorbent that the obtained results are presented in Table 1. In the Langmuir model, a plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/(K_L \cdot q_m)$ (Fig. 9A). K_F and n are empirical constants

of the Freundlich model which indicate the adsorption capacity and adsorption intensity and can be calculated from the slope and intercept of the linear plot (Fig. 9B). The correlation coefficient showed good positive evidence on the adsorption of Cd^{2+} onto the adsorbent ($R^2=0.9977$) follows the Langmuir isotherm. The maximum monolayer capacity q_m and K_L the Langmuir constant were calculated from the Langmuir as 5.1867 mg/g and 0.1562 L/mg, respectively. Based on the correlation coefficient (R^2), the fit of the data for Cd^{2+} adsorption onto the adsorbent suggests that the Langmuir model ($R^2=0.9977$) gave better fitting than that of the Freundlich model ($R^2=0.9874$). It may also be concluded from these data that the surface of the adsorbent is made up of homogenous adsorption patches than heterogeneous adsorption patches [32, 39]. The exponent n of 1.7863 is in the

Table 1. Langmuir and Freundlich model correlation coefficients and constants for adsorption of Cd^{2+} on the adsorbent at ambient temperature.

Model	Parameters		
	q_m (mg/g)	K_L (L/mg)	R^2
Langmuir	5.1867	0.1562	0.9977
Freundlich	K_F (mg/g)/(L/mg) ⁻ⁿ	N	R^2
	0.8350	1.7863	0.9874

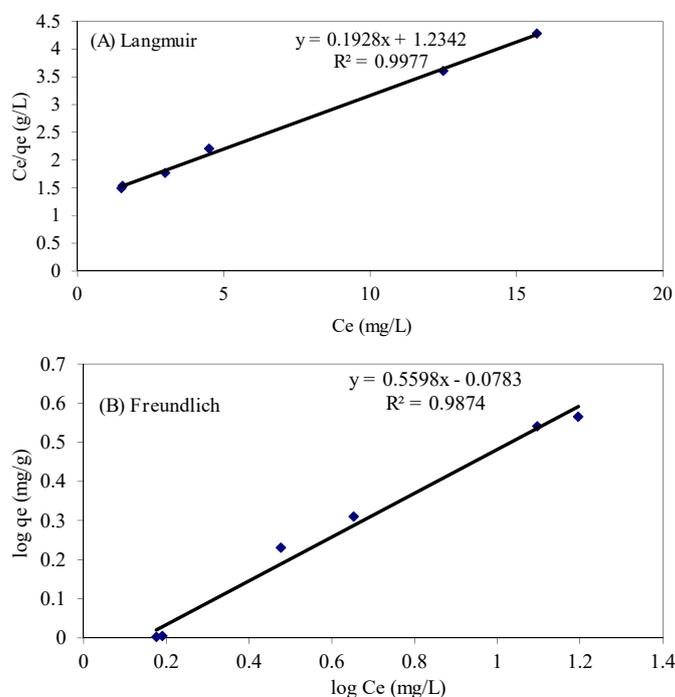


Fig. 9. Langmuir (A) and Freundlich (B) isotherm models for the adsorption of Cd^{2+} on the adsorbent.

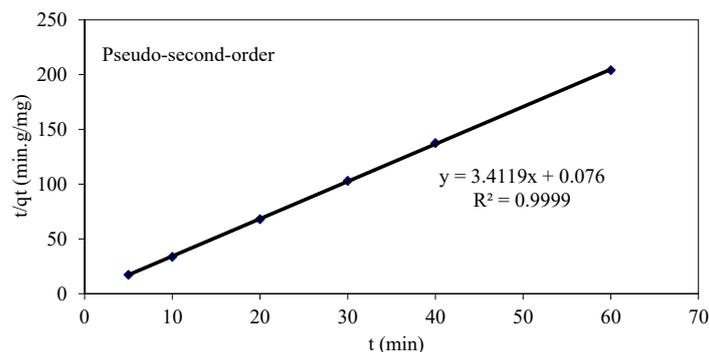


Fig. 10. Sorption kinetics fitted by pseudo-second order of Cd^{2+} onto the adsorbent in solution.

range of 1–10, indicating a favorable adsorption [16, 32]. These results indicate that the adsorbent developed in the current study has great potential for the removal of Cd^{2+} from contaminated water.

Adsorption kinetics

To study the rate of adsorption [13], its mechanism, and its potential rate-controlling steps that include mass transport and chemical reaction processes [29], the kinetic data were fitted by the pseudo-second-order model (Fig. 10), since it has been shown to be appropriate for many sorption processes [13, 14, 28, 33].

It can be seen that the R^2 value of the pseudo-second-order model is 0.9999. Moreover, the calculated equilibrium adsorption capacities (q_e values) of the pseudo-second-order model are closer to the experimental data. These results indicated that the Cd^{2+} adsorption processes followed a second-order type kinetic reaction, which suggests that the adsorption rate in the solutions was probably limited by chemisorption, and the adsorption probably takes place via surface complexation reactions at specific sorption sites [29, 40]. In the other words, it suggested the multi-step process involving sorption on the external surface and diffusion into the interior of adsorbent, or the process could be chemisorption through valency force by sharing or by exchange of electron between the adsorbent and Cd^{2+} ions [13].

CONCLUSION

In this study, a sulfur-modified magnetic nanoparticle was synthesized as an adsorbent for the removal of Cd^{2+} ions from aqueous solutions. SEM micrograph of the adsorbent depicted the morphological characteristics favorable for metal adsorption. The functional groups and surface

properties of the adsorbent were confirmed by the FT-IR spectra and TGA. The optimum pH, contact time, and initial concentration of Cd^{2+} in the batch adsorption studies were 5, 10 min, and 10–30 mg/L, respectively. The equilibrium data fitted the Langmuir isotherm model better than the Freundlich isotherm model, and the maximum monolayer capacity q_m and K_L the Langmuir constant were calculated from the Langmuir as 5.1867 mg/g and 0.1562 L/mg, respectively. The results were well explained in terms of pseudo-second-order kinetics, which suggests that the adsorption rate in the solutions was probably limited by chemisorption, and the adsorption probably takes place via surface complexation reactions at specific sorption sites. These results indicate that the adsorbent developed in the current study has great potential for the removal of Cd^{2+} from contaminated water.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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