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Removal and recovery of cadmium from aqueous solutions using magnetic nanoparticle-modified sawdust: kinetics and adsorption isotherm studies

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ABSTRACT

Removal and recovery of Cd(II) was studied on sawdust modified with magnetic nanoparticles, Fe_3O_4 (MNP), from aqueous solution. MNP were prepared, loaded on sawdust, and characterized using scanning electron microscopy and surface area analyzer. The parameters for removal percentage of Cd(II) from aqueous solutions were studied such as pH, contact time, and concentration of Cd(II). Results for kinetics studies revealed that Cd(II) removal followed pseudo-second-order kinetics and the q_e calculated values (22.17 mg g^{-1}) were in close agreement with experimental values (22.45 mg g^{-1}) with a high value of correlation coefficient ($R^2 = 0.9994$). The adsorption isotherm data were followed by Langmuir isotherm model adsorption studies. The adsorption capacity (Q_o) was found to be 1,000 mg g^{-1}, 588.5 mg g^{-1}, and 403.7 mg g^{-1} for SD-MNP, MNP, and SD, respectively.

Keywords: Sawdust; Magnetic nanoparticles; Cd(II); Adsorption kinetics; Adsorption isotherm

1. Introduction

Contamination of water with toxic metal ions (Pb(II), Cd(II), Cr(VI), Hg(II), Co(II), Cu(II), Ni(II), and As(III)) is becoming a severe environmental and public health problem [1,2]. The effluents of industries such as smelting, metal plating, Cd–Ni batteries, phosphate fertilizers, mining, paints, pigments, plastics, stabilizers, alloy industries, ceramics, and sewage sludge are mostly responsible for the introduction of Cd(II) into water [3]. Cd(II) causes significant physiological disorders such as damage of central nervous system and blood composition, production of energy, and irreversible damage of vital organs of the body [1]. Therefore, different chemical, biological, biochemical, and physicochemical methods have been used to remove heavy metals from wastewaters and groundwater.

To achieve environmental detoxification, various techniques such as ion exchange, coagulation, flotation, coprecipitation, electrochemical treatments, adsorption, and membrane filtration have been mostly used. Among these, adsorption is one of the promising processes used to remove toxic metal ions from water due to high adsorption capacity and selectivity. Different adsorbents either waste material such as activated coconut shell carbon [4], mango peel waste [5], sawdust [6], chitosan [7] or synthetic such as zeolites [8], hydroxides [9], hydroxyapatite [10], diatomite [11], cysteine-modified biomass [12], and synthetic polystyrene resin [13] were used for the removal of heavy metals from aqueous solution. Synthetic adsorbents

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have certain limitations such as running cost, waste disposal, and low removal efficiency. Recently, nanoadsorbent such as zinc oxide nanoparticles [14], nano-alumina [15], functionalized carbon nanotubes [16], functionalized silica nanoparticles [17], and hydroxyapatite nanoparticles [1] have been studied for the removal of metal ions.

As the nanoadsorbent has certain advantages over simple adsorbent, simple magnetic nanoparticles (MNP) (Fe_3O_4) [18], humic acid functionalized and stabilized Fe_3O_4 nanoparticles [19], amino-functionalized nanoparticle [20], and orange peel modified with MNP [21] have been used as adsorbent for heavy metals removal from aqueous solution. The objective of the present work was to develop a nanoparticle-based method for the removal and recovery of trace amount of cadmium. The method was based on adsorption of cadmium on magnetic nanoparticles-modified sawdust. The effect of pH, time, and concentration of metal ion was studied on the adsorption of Cd(II).

2. Materials and methods

2.1. Reagents

All chemicals used were of analytical reagent grade or similar purity. Cadmium(II) nitrate hexahydrate [$Cd(NO_3)_2{\cdot}6H_2O$], ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), and ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) were supplied by BDH laboratories, BH15 ITD England. Ammonia solution (35%), hydrochloric acid (37%), sodium hydroxide, boric acid, phosphoric acid, and acetic acid were supplied by Riedel-deHaen Sigma-Aldrich.

2.2. Adsorbent

Mulberry wood sawdust collected from the local saw mill was washed with distilled water to remove any dirt and dried in oven at 80˚C for 6 h. The dried material was ground, passed through a sieve with particle size <355 μm using standard sieve, and stored in air tight bottle for further use. MNP and magnetic nanoparticles-loaded sawdust (SD-MNP) were prepared by modified coprecipitation method [21,22]. Briefly, 6.3 g of $FeCl_3{\cdot}7H_2O$ and 4.2 g of $FeSO_4{\cdot}7H_2O$ was dissolved in 200 mL of distilled water and stirred at 80˚C under nitrogen atmosphere. Black precipitates of MNP were formed when 20 mL of 25% ammonia solution was added. For loading of MNP on sawdust, 10 g of SD was added to the solution at 80˚C for 60 min under vigorous stirring. The resultant SD-MNP was filtered, washed with distilled water until the pH of filtrate became neutral, and dried in oven at 70˚C. The SD-MNP obtained was checked for its magnetic property with magnetic rod, and it was observed that adsorbent was attracted toward magnetic rod.

2.3. Adsorbent characterization

Surface morphology was analyzed using 30 kV Scanning Electron Microscope (JSM5910, JEOL, Japan). The BET and BJH surface area, pore volume, and pore size of the adsorbents were analyzed by Surface Area Analyzer NOVA Quantachrome, USA.

2.4. Batch adsorption studies

Batch adsorption studies using three adsorbents (SD-MNP, MNP, and SD) were carried out in aqueous solution. In adsorption process, 100 mg of each adsorbent was placed in a conical flask in which 20 mL of Cd(II) solution of the desired concentration (50–250 mg L^{-1}) was added. All the mixtures were agitated at 150 rpm (Orbital shaker, OS-340C, digisystem laboratory instrument Inc., Made in Taiwan). The SD adsorbent was separated through filtration, while SD-MNP and MNP were separated with external magnet. The final concentration of metal ion unadsorbed was determined by Atomic Absorption Spectrophotometer (Perkin Elmer model AA200, USA). The effect of initial pH on the adsorption of Cd(II) was studied by adjusting pH to 3, 4, 5, 6, and 7. The pH was adjusted to the desired value by addition of Britton–Robinson buffer solution [23].

For determination of percent adsorption and adsorption capacity, the following two equations were used.

$$\text{Percent adsorption of Cd(II)} = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

$$\text{Adsorption capacity } q_e = \left[\frac{C_i - C_f}{m}\right] V \tag{2}$$

where C_i and C_f are the initial and final concentration of Cd(II), q_e is the adsorption capacity in mg g^{-1}, V is the volume of Cd(II) in mL, and m is the mass of adsorbent in grams. All the experimental studies were performed in triplicate, and average results were reported.

2.5. Adsorption kinetics

SD-MNP, MNP, and SD (100 mg) were added to 20 mL (200 mg L^{-1}) solution of Cd(II). The mixture was agitated at 150 rpm. In order to study the mechanism of adsorption kinetics, pseudo-first-order and pseudo-second-order kinetics and intraparticle diffusion model were used to evaluate the kinetic data of Cd(II) adsorption onto SD-MNP, MNP, and SD. For the pseudo-first-order kinetics, the following equation was used:

$$\log\,(q_e - q_t) = \log\,q_e - \frac{K_1 t}{2.303} \tag{3}$$

where q_t and q_e are the adsorption capacities at time t (min) and at equilibrium time, and k_1 is the rate constant for pseudo-first-order kinetics of the adsorption process. The values of q_e and k_1 were calculated from the pseudo-first-order model.

For the pseudo-second-order kinetics, the following equation was used:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \tag{4}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively; k_2 is rate constant for pseudo-second-order kinetics. The values of k_2 and q_e were calculated from pseudo-second-order model.

For the evaluation of intraparticle diffusion in the adsorption process of Cd(II) on MNP-SD, SD, and MNP, the following equation was used to describe the intraparticle diffusion model.

$$q_t = K_{\text{int}} t^{1/2} + C \tag{5}$$

where C is the intercept and related to the thickness of the boundary layer, and K_{int} (mg g^{-1} min$^{-1/2}$) is the intraparticle diffusion rate constant. The values of these constants were calculated directly from the intercept and slope of the graph.

2.6. Adsorption isotherm

SD-MNP, MNP, and SD (100 mg) adsorbents were added to 20 mL of Cd(II) solution at the concentration range from 50 to 250 mg L^{-1}. The mixtures were agitated at 150 rpm for 60 min to study the adsorption isotherm. In this study, adsorption data were explained by the widely used models of Langmuir and Freundlich isotherms.

The Langmuir isotherm assumes monolayer adsorption of the adsorbate on a homogeneous surface of the adsorbent.

The linear form of the Langmuir model used for analysis is as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \tag{6}$$

where C_e is the equilibrium concentration (μg mL^{-1}), q_e is the amount of solute adsorbed per gram of adsorbent; K_L and a_L are the Langmuir adsorption isotherm constants and are related to the maximum capacity (L g^{-1}) and bonding strength (L mg^{-1}), respectively. The theoretical monolayer capacity is Q_o and is numerically equal to K_L/a_L.

Freundlich isotherm is used for adsorption of adsorbate on heterogeneous surface of the adsorbent. The linear form of Freundlich equation used is as follows:

$$\log\,q_e = \log\,K_F + \frac{1}{n}\log\,C_e \tag{7}$$

where K_F is the Freundlich adsorption isotherm constant (mg g^{-1}), $1/n$ (g L^{-1}) is a measure of the adsorption intensity or the heterogeneity factor, and n is the measure of the deviation from linearity of adsorption. Its value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if the value of n is equal to unity, it indicates linear adsorption; if the value is below unity, then it indicates chemical adsorption, and if it is above unity, it shows physical adsorption process. While q_e is the amount adsorbed (mg g^{-1}), and C_e is the equilibrium concentration (μg mL^{-1}).

2.7. Effect of coexisting cations

The multimetal cation adsorption of nanoadsorbent was studied in the presence of Na^+, K^+, Ca^{2+}, and Mg^{2+}. A sample containing a mixture of Cd(II) with the respective cations was prepared at pH 7. The concentration of Cd(II) was maintained at 200 mg L^{-1}, and the cation concentration was changed from 200 to 1,000 mg L^{-1}.

2.8. Desorption study

Adsorption study was performed by mixing 100 mg of adsorbent (SD-MNP) with 20 mL of 100 mg/mL Cd(II) solution. The pH of the solution was adjusted to 7 using buffer solution, and the mixture was agitated at 150 rpm for 30 min. Then Cd (II)-loaded SD-MNP was separated with magnet.

Desorption studies were performed on loaded SD-MNP in batch using 10 mL of 0.1 M of HCl, HNO_3, and NaOH. The mixture was agitated for 120 min. All the adsorption and desorption experiments were carried out at room temperature. The amount of Cd(II) desorbed in the eluent solution was determined with AAS.

3. Results and discussion

The effect of different adsorption variables such as pH, contact time, Cd(II) concentration, and coexisting ions was studied for maximum adsorption of Cd(II) on SD-MNP and compared with MNP and SD as adsorbents.

3.1. Effect of pH

The effect of pH on the adsorption of Cd(II) was studied in the range of 3–7 on SD-MNP, MNP, and SD as adsorbent at room temperature (Fig. 1). The point of zero charge (pzc) pH of SD-MNP was determined according to the method reported in the literature [24] and was found to be 6.0 for SD-MNP. At pH < pHpzc, the SD-MNP particles are positively charged, while at pH > pHpzc, the SD-MNP particles are negatively charged. The percent removal of Cd(II) was lower at low pH because of the higher concentration of hydronium ions and its higher mobility due to smaller size. Below pHpzc, the surface of the adsorbent is positively charged and prevents the adsorption of positively charged Cd(II). At optimum pH 7, the concentration of hydronium ions is reduced and the adsorption of Cd(II) increased. At higher pH than the optimum pH, the hydroxyl ion concentration increased and Cd(II) formed hydroxide which decreased the concentration of Cd(II). At optimum pH, SD-MNP and MNP showed higher percent adsorption of 98% and 90%, respectively, whereas the SD showed only 50% adsorption at optimum pH 6. Same mechanism and results have also been reported by Gupta and Nayak [21]. The Cd(II) adsorption onto SD-MNP, MNP, and SD is mainly governed by physicochemical process. The dependence of adsorption on pH suggests that ion exchange mechanism followed by Cd(II) due to the ionic interaction of the Cd (II) ions with the deprotonated form of SD-MNP.

3.2. Effect of contact time on adsorption

The effect of contact time on adsorption of Cd(II) ions was studied from 10 to 60 min at 150 rpm agitation speed (Fig. 2). The percent adsorption increased rapidly in the initial 10 min, in case of SD-MNP and SD equilibrium were established in 30 min with maximum adsorption of 98 and 76%, respectively. While in case of MNP, the equilibrium was established in 50 min with maximum adsorption of 100%.

3.3. Effect of coexisting cations

The effect of different coexisting cations of alkali and alkaline earth metals such as Na^+, K^+, Ca^{2+}, and Mg^{2+} were studied on the adsorption of Cd(II) on SD-MNP, MNP, and SD as shown in Fig. 3. It can be seen from the result that the presence of these coexisting cations have negligible effect on adsorption of Cd (II) on SD-MNP, MNP, and SD up to 1,000 µg. It can be concluded from the study that the adsorption of Cd(II) on SD-MNP, MNP, and SD is highly selective.

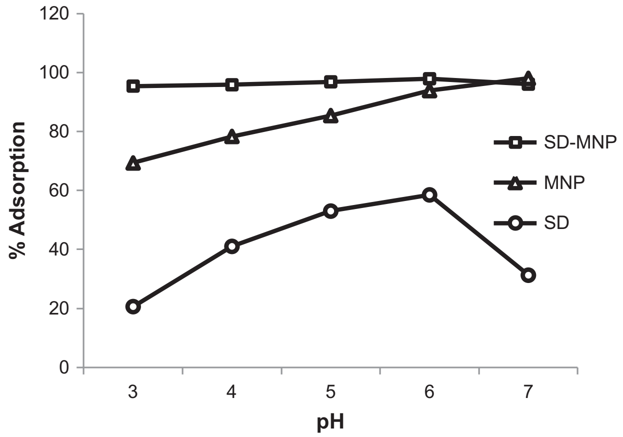

Fig. 1. Effect of pH on Cd(II) adsorption using SD-MNP, MNP, and SD.

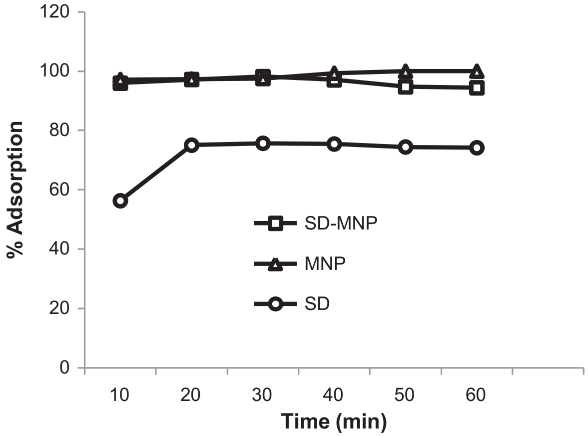

Fig. 2. Effect of time on adsorption of Cd(II) using SD-MNP, MNP, and SD.

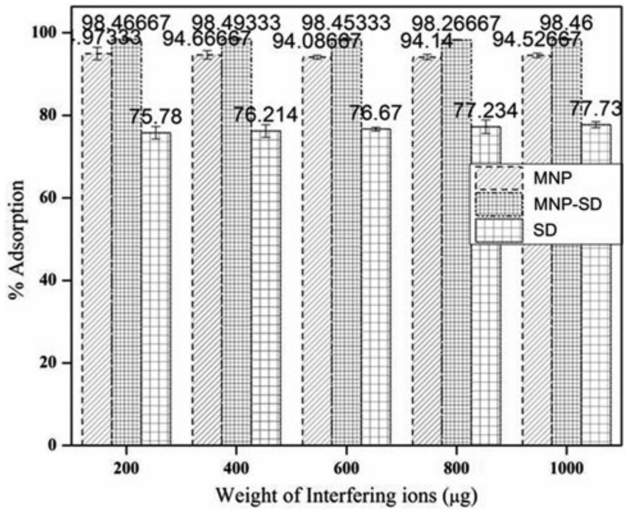

Fig. 3. Effect of coexisting cations on adsorption of Cd(II) onto SD-MNP, MNP, and SD.

3.4. Kinetic studies

Batch adsorption studies are important for the design of adsorption column on large scale for industries. Nature of the adsorption process depends on the chemical and physical characteristics of adsorbent as well as on the conditions of the system. For the study of adsorption kinetics of Cd(II) onto SD-MNP, MNP, and SD, the pseudo-first-order and pseudo-second-order kinetic models were studied (Eqs. (3) and (4)). Pseudo-first-order kinetic model gave a straight line with smaller correlation coefficient value (R^2) of 0.516, 0.734, and 0.968 with SD-MNP, MNP, and SD, respectively (Table 1). Moreover, lower values of calculated adsorption capacity (q_e) predicted than experimental values which indicated that pseudo-first-order kinetic model is not applicable. Then, the experimental adsorption data were analyzed by pseudo-second-order kinetic model (Fig. 4). The values of k_2, q_e, and R^2 were calculated from the plot, and the results are shown in Table 1. The linear correlation coefficient (R^2) values of pseudo-second-order kinetic model are higher than the pseudo-first-order kinetic model for adsorption study onto SD-MNP, MNP, and SD. The adsorption capacity (q_e) values calculated are also close to q_e experimental values. Therefore, it can be concluded that good correlation for the adsorption of Cd(II) ions on SD-MNP, MNP, and SD can be obtained by the use of pseudo-second-order kinetic model. Similar results for kinetic studies were reported in the literature [7,25–28].

For the control of adsorption system, it is required to study the mechanism under which the dynamic behavior of the system results. The adsorption of Cd (II) ions onto SD-MNP, MNP, and SD adsorbents was found rapid at initial contact time and then become constant when the contact time was increased. In a solid/liquid adsorption process, the transfer of solute is characterized by boundary layer diffusion and intraparticle diffusion. The technique is commonly used to identify the adsorption plot (Eq. (5)). The plot of q_t (mg g^{-1}) vs. $t^{1/2}$ is shown in Fig. 5. The plot shows multilinearity in the adsorption process with three steps of adsorption. It suggests that the adsorption processes mainly due to surface diffusion and intraparticle diffusion. The C values of all the three adsorbents were found positive indicating the effect of boundary layer diffusion (Table 1), and the value was higher both for SD-MNP and MNP (20.75 mg g^{-1}), but lower value of C (3.04 mg g^{-1}) was observed for SD, which indicated that the adsorption capacity of SD-MNP and MNP is close to the experimental value (Table 1). The same type of multilinearity in the intraparticle diffusion plots have also been reported by

Table 1
Parameter of the pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models

		Adsorbents		
Kinetic models	Parameters	SD-MNP	MNP	SD
Pseudo-first-order model	q_e (exp) (mg g^{-1})	22.45	21.81	11.7
	k_1 (min^{-1})	0.017	0.048	0.09
	q_e (mg g^{-1})	1.16	0.80	13.24
	R^2	0.516	0.734	0.968
Pseudo-second-order model	k_2 (min^{-1})	0.147	0.13	0.004
	q_e (mg g^{-1})	22.17	21.92	16.39
	R^2	0.9994	1.000	0.988
Intraparticle diffusion model	K_{int} (min^{-1})	0.18	0.147	1.365
	C (mg g^{-1})	20.75	20.75	3.04
	R^2	0.506	0.779	0.87

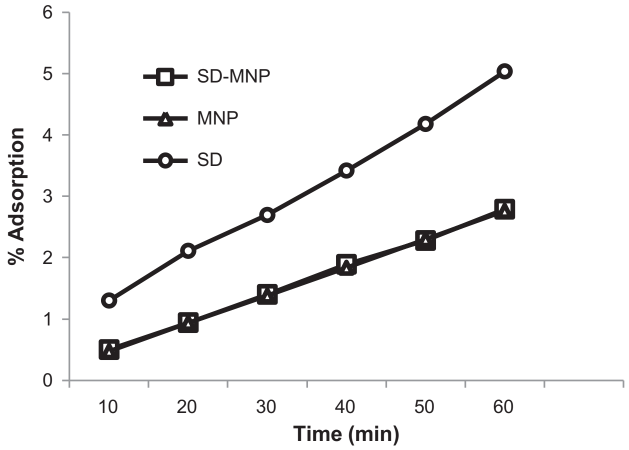

Fig. 4. Pseudo-second-order kinetic model for Cd(II) adsorption.

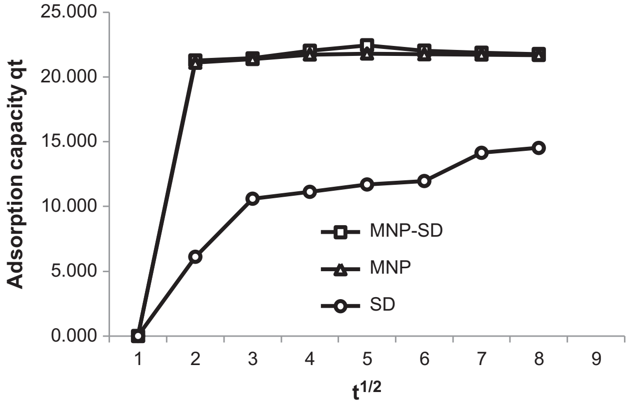

Fig. 5. Intraparticle diffusion model for different adsorbents.

Ofomaja [25] for Cu(II) adsorption on Mansonia sawdust and Shah et al. [27] for adsorption of Ni(II) on waste tea leaves. The existence of multistep in the plot indicated that during adsorption process, some other adsorption mechanism such as ion exchange or complexation may control the rate.

3.5. Adsorption isotherm

The adsorption isotherm is important to describe the interpretation of adsorbate with adsorbent and also for the information of adsorption capacity of an adsorbent. The surface of the adsorbent may act as a monolayer or multilayer. The Langmuir adsorption isotherm model is used for monolayer adsorption of adsorbate from liquid solution on a surface of adsorbate containing finite number of identical sites. The isotherm data are given in Table 2. The data fitted well to the Langmuir model with correlation coefficients (R^2) of 0.9984, 0.9457, and 0.9283 for SD-MNP, MNP, and SD, respectively. Maximum adsorption capacity (Q_o) was to be found 1,000 mg g^{-1} for SD-MNP. The a_L values (L mg^{-1}) showed an ascending order of affinity to the SD, MNP, and SD-MNP as follows: SD-Cd (1.57) > MNP-Cd (1.9) > SD-MNP-Cd (2.0). High adsorption capacity area of nano-size particles as well as the hydroxyl functional groups of SD; both of which provided in a combined form, effective sites for Cd(II) ions binding.

Table 2
Comparison of parameters of different isotherm models

		Adsorbents		
Isotherm models	Parameters	SD-MNP	MNP	SD
Freundlich	K_F (mg g^{-1})	354.8	295.17	0.33
	n	1.62	5.68	4.83
	$1/n$	0.6162	0.1759	0.2
	R^2	0.8818	0.8778	0.8224
Langmuir	a_L (L mg^{-1})	2.0	1.9	1.57
	K_L (L g^{-1})	2,000	625	3.46
	Q_o (mg g^{-1})	1,000	588.51	403.74
	R^2	0.9984	0.9457	0.9283

The Freundlich adsorption isotherm model explains the multilayer adsorption by assuming interaction of adsorbed molecules on a heterogeneous surface with a nonuniform distribution of adsorption heat. As can be seen from Table 2, K_F value of SD-MNP (354.8 mg g^{-1}) is greater than MNP and SD. Poor values of correlation coefficients (R^2) indicate inapplicability of Freundlich isotherm. The Langmuir isotherm model gave better fit than Freundlich as indicated by values of correlation coefficients. Similar results have been reported by Gupta and Nayak [21]. The adsorption intensity $1/n$ values for SD-MNP, MNP, and SD are >0.05 indicating a strong bond formation between the adsorbate and the adsorbent during the adsorption process.

3.6. Desorption

The desorption studies are helpful to elucidate the adsorption mechanism, recovery of adsorbate, and recycling of adsorbent. The desorption of Cd(II) on loaded SD-MNP was carried out with 0.1 M HNO_3, and about 97% of the adsorbed Cd(II) was recovered. Adsorption–desorption process was repeated and, after four consecutive processes, a small decrease was observed. This may be attributed to damage of original surface layer of iron oxide when the extraction of Cd(II) from SD-MNP proceeds through acid

Table 3
Removal of Cd(II) ions from various water samples

Adsorbent	Sample	Cd(II) added (μg)	% Adsorption
MNP	Tap water	100	98.400
		300	99.278
	River Kurram	100	98.800
		300	96.167
	River Tochi (NWA)	100	97.317
		300	97.113
MNP-SD	Tap water	100	95.068
		300	96.989
	River Kurram	100	96.167
		300	94.844
	River Tochi (NWA)	100	96.033
		300	95.200

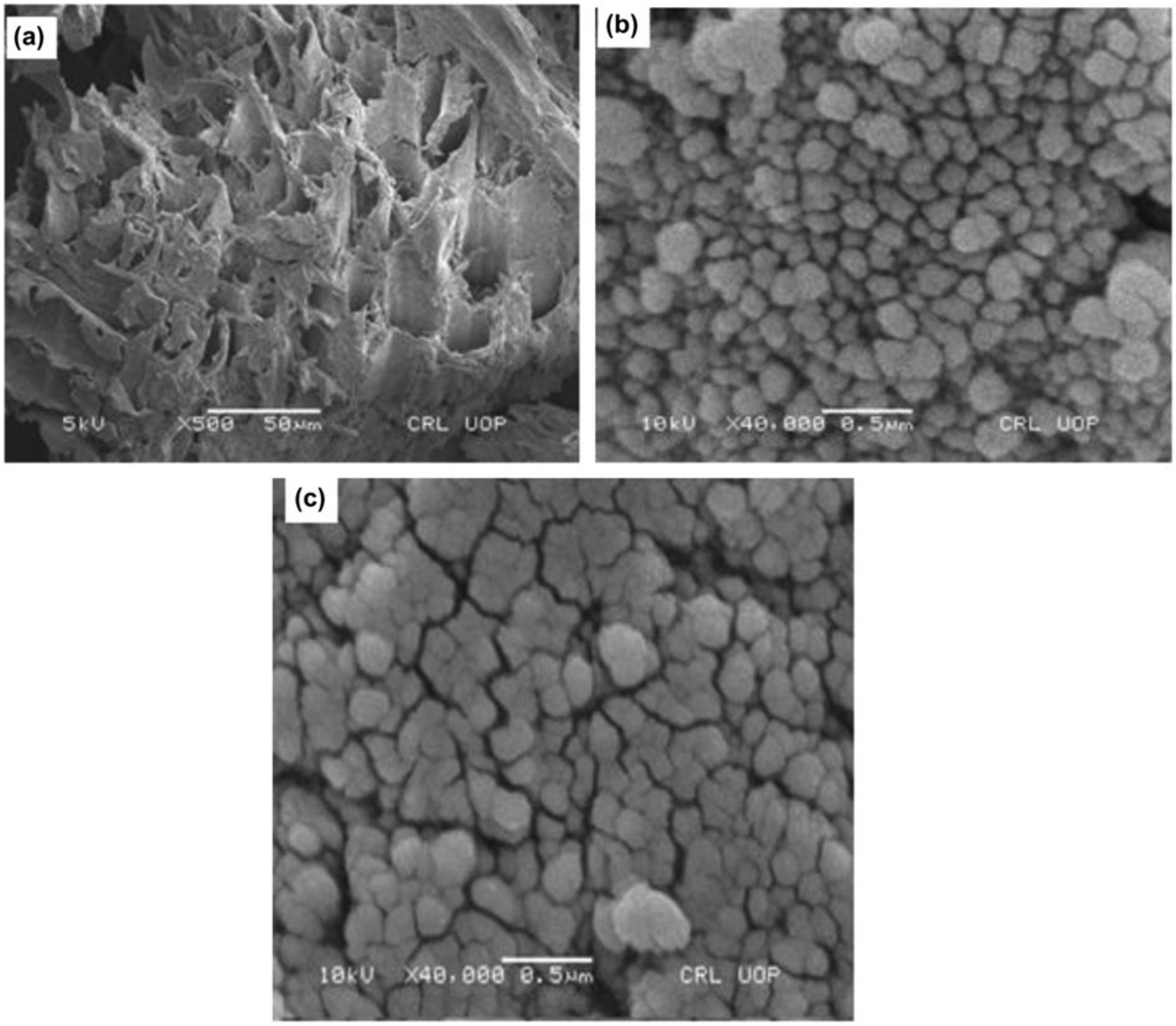

Fig. 6. SEM images of adsorbents (a) SD, (b) MNP, and (c) SD-MNP.

Table 4
Surface area, pore size, and pore volume by BET and BJH methods

Sample	Method	Surface area ($mg^2 g^{-1}$)	Pore volume (ccg^{-1})	Pore size (Å)
MNP	BET	80.14	0.21	44.23
	BJH	104.9		
SD-MNP	BET	51.36	0.15	135.7
	BJH	64.88		
SD	BET	36.07	0.13	131.85
	BJH	47.5		

desorption process [29,30]. The iron in the desorbed eluent was also determined by AAS and found that there was no obvious iron ions in the eluent. This indicates that the dissociation of Fe_3O_4 during desorption process was not an issue.

3.7. Application to real samples

The proposed method was used for the removal of Cd(II) from tap water and river water collected from various areas of Pakistan as shown in Table 3. Standard addition method was used in which 10 mL of the water sample was taken, spiked with known amount of Cd(II), and after adsorption process, percent removal of Cd(II) was determined. It can be seen from Table 3 that the removal efficiency of Cd(II) from the water samples by SD-MNP and MNP is high and can be used successfully for the removal of Cd(II) from real water sample.

3.8. Characterization

Scanning electron microscopy (SEM) is an important technique for visual confirmation of physical nature of the surface and its morphology. The SEM images of SD-MNP, MNP, and SD are given in Fig. 6. It is clear from the figure that surface morphology of sawdust changed after modification with MNP. The hollow spheres in sawdust were covered by MNP.

N_2 adsorption/desorption method was used for BET and BJH surface area, pore size, and pore volume of the adsorbents (SD-MNP, MNP, and SD). The results are given in Table 4. The BET surface area of SD increased after modification with MNP from 36.07 to 51.36 $mg^2 g^{-1}$. The same is in the case of pore volume and pore size increased from 0.13 to 0.15 ccg^{-1} and 131.85 to 135.72 Å, respectively.

4. Conclusion

In the present study, removal of Cd(II) from aqueous solution was carried out using SD-MNP and the removal efficiency was compared with MNP and SD. Kinetic models show that the data fit to the pseudo-second-order kinetic model for SD-MNP, MNP, and SD. The adsorption of Cd(II) follows Langmuir adsorption isotherm and gave better fitting with experimental data than Freundlich isotherm model. The effect of coexisting cations (Na^+, K^{++}, Ca^{++}, and Mg^{++}) shows that the presence of these coexisting cations have no effect on the adsorption of Cd(II) on SD-MNP, MNP, and SD. Desorption studies are also fulfilling the criteria of advance adsorbents. It can be concluded that SD-MNP has a high adsorption capacity and rapid kinetics as well as with the significance of easy synthesis, low cost, simple to recover, and environment friendly. Therefore, SD-MNP can be used for environmental water cleanup processes as an advanced adsorbent.

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