Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.21057

83 (2017) 123–132
July

Magnetic solid phase extraction of Cd (II) using magnetic nanoparticle (MNPs) and silica coated magnetic nanoparticles (SiMNPs) from environmental water samples

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Received 4 February 2017; Accepted 17 June 2017

ABSTRACT

In the present study synthesis of magnetic nanoparticle (MNPs) and silica coated magnetic nanoparticle SiMNPs were carried using co-precipitation method and used for the sold phase extraction of Cd (II) from environmental water samples. MNPs and SiMNPs were characterized using FTIR for surface functional group, SEM for surface morphology, EDX for elemental analysis and SAA for surface area, pore volume and pore size. For quantitative percent recovery various analytical parameter like solution pH, adsorbent dose, volume of sample, eluent type and volume and matrix effect were optimized. Limit of detection (LOD) like 0.30 µg L^{-1} and 0.31 µg L^{-1} for SiMNPs and MNPs values shows that the method is highly sensitive. The kinetic data shows that the adsorption of Cd (II) on MNPs and SiMNPs follows pseudo second order kinetics. Values of ΔH°, ΔS° and ΔG° show that these adsorption processes are exothermic and feasible in nature. For equilibrium studies different isotherms like Langmuir, Freundlich, Temkin and D-R adsorption isotherms were applied. The method was successfully applied to environmental water samples like Tap water and River water with satisfied recovery results.

Keywords: Solid phase extraction; Magnetic nanoparticle; Co-precipitation; Preconcentration

1.Introduction

Heavy metals like cadmium, mercury, arsenic, nickel, copper, lead and cobalt are toxic in nature to human, animal and plants even at trace level due to its bioaccumulation and non-biodegradability [1,2]. The main sources that introduced cadmium into water streams are various industries like, smelting, metal plating, Cd–Ni batteries, phosphate fertilizers, paint, pigments, plastics, stabilizers, alloy industries, ceramics, etc. [3]. Cadmium is carcinogenic according to IRAC (1987) and also causes chromosomal aberration. Therefore the accurate determination of these heavy metals at trace level in a complex environmental sample is one of the challenging tasks for analytical chemist. As the concentration of these heavy metals is very low in real water samples then the analytical detection system, therefore the direct determination of these heavy metals by using sophisticated analytical technique like flame and graphite furnace atomic absorption spectrometry (FAAS/GFAAS), microwave plasma-atomic emission spectroscopy (MP-AES) [4], inductively coupled plasma-optical emission spectrometry (ICP-OES) [5], inductively coupled plasma-mass spectrometry (ICP-MS) and electroanalytical technique is not possible [6,7]. Therefore, for the accurate determination of trace metals need proper preconcentration step prior to its analytical determination [8–13].

Large number of analytical extraction technique like dispersive liquid-liquid extraction (DLLE) [9], head space liquid phase extraction (HSLPE) [14], cloud point extraction (CPE) [15], in-situ solvent formation extraction (ISFE) [16], ultrasound ionic liquid based dispersive liquid extraction (UILBDLE) [17], co-precipitation [18], switchable solvent based liquid extraction (SsLE) [19] and solid

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phase extraction [20] were employed for the preconcentration of heavy metals from environmental samples by different researchers in the last few years. Due to certain advantages like low running cost, high recovery, short extraction time and low consumption of organic compound, solid phase extraction is still a better technique for the extraction of heavy metals from environmental water samples [6,21,22].

In the last few decades nanotechnology has attracted great intention of the scientist due to its unique properties [23]. The nanometer size particle are 1 nm to 100 nm in diameter, having large surface area, large surface-to-volume ratio and thus having large adsorption capacity [23]. Magnetic nanoparticle are super-paramagnetic and attracted toward the magnetic field having large number of application like cell labeling in biotechnology, magnetic resonance imaging, protein and enzyme separation [23]. Iron-oxide magnetic nanoparticles like Fe_3O_4 and Fe_2O_3 have been showing a wide-reaching research interest as they have unique size-dependent characteristics that strongly differ from the properties of the corresponding bulk material and enable them to be used for various applications [24]. Moreover magnetic nanoparticle have can be separated by using external magnetic field without agglomeration to avoid the sample loss during filtration [20,25]. Iron oxide magnetic nanoparticle can be successfully used for the removal of heavy metal like Cr (III) [26], As (V) [27] and Cd (II) [2] from the aqueous solution. Pure inorganic magnetic nanoparticle form large aggregates and also not selective [20,28]. In order to overcome these limitation the surface of the magnetic nanoparticle were coated with silica to form silica coated magnetic nanoparticle (SiMNP) because silica is one of the most ideal shell materials due to its consistent chemical stability and flexibility in surface modification via Si–OH groups [29].

In the present study magnetic nanoparticles (MNPs) have been synthesized by using co-precipitation method. The magnetic nanoparticles synthesized were treated with Tetraethoxysilane (TEOS) to obtained silica coated magnetic nanoparticle (SiMNPs).The MNPs and SiMNPs were employed for the solid phase extraction of Cd (II) from aqueous solution and the extraction efficiency of MNPs and SiMNPs were compared. Kinetics, thermodynamic and equilibrium studies were also carried out to this solid phase extraction studies.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical reagent grade or similar purity. Stock solution of metal ion was prepared by diluting standard solution of Cadmium (II) purchased from E. Merck Company (Darmstadt, Germany). For the preparation of magnetic nanoparticles salts, ferric chloride hexahydrate $FeCl_3{\cdot}6H_2O$, and ferrous sulphate 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. Tetraethoxysilane was supplied by Alfa Aesar a John Matthey Company. Different combination of acids and salts: phosphate buffer solution (pH 2–4, sodium dihydrogen phosphate/phosphoric acid), acetate buffer solution (pH 5.0–7.0 acetic acid and ammonium acetate), ammonia buffer solution (pH 8.0, ammonia/ammonium chloride) and phosphate buffer solution (pH 9.0 and pH 10, sodium phosphate) were used to obtain the required pH of the sample solution.

2.2. Instruments

A Perkin-Elmer flame atomic absorption spectrometer Model AA 200 having (air–acetylene flame, 10 cm long-slot burner head and hollow cathode lamp was used as radiation source) was used for absorbing measurement of the entire Cd (II) samples. The measurements were performed with the continuous aspiration mode of FAAS. A pH-meter with glass electrode of model (422-WTW, Weilheim) was used for pH measurements. The solid phase was separated by using Nd magnet. Vortex mixer (Wiggen Hauser, Malaysia) was used for homogenous mixing of solutions.

FT-IR spectra of the adsorbent were carried by using IR Prestigue-21 SHIMADZU HK in the range of 4000 cm^{-1} to 500 cm^{-1}. For surface morphology of the adsorbent the SEM images were obtained by using 30 KV SEM and EDX (JSM5910, JEOL, Japan). The surface area, pore volume and pore width of adsorbent was determined by the BET-N_2 method using a surface area analyzer NOVA Quantachrome USA.

2.3. Preparation of silica-coated magnetic nanoparticle

Silica-coated magnetic nanoparticles were prepared in two steps. In the first step Fe_3O_4 were prepared by using co-precipitation method with minor modification in which salt of Fe^{2+} (4.2 g $FeSO_4{\cdot}7H_2O$) and salt of Fe^{3+} (6.3 g of $FeCl_3{\cdot}6H_2O$) were mixed in 200 mL of distilled water with vigorous stirring at 80°C under nitrogen atmosphere. Black precipitates of Fe_3O_4 were formed when 20 mL of 25% ammonia solution was added. The Fe_3O_4 obtained were washed twice with distilled water, dried at 100°C, checked for its magnetic property with magnetic rod (Fig. 1).

$$\begin{aligned} &FeSO_4\cdot 7H_2O + 2FeCl_3\cdot 6H_2O + 8NH_4OH \rightarrow Fe_3O_4 \\ &\quad + 6NH_4Cl + (NH_4)_2SO_4 + 17H_2O \end{aligned} \tag{1}$$

Magnetic nanoparticles (4 g) were re-dispersed in 150 mL of ethanol and 50 mL of water. To obtained pH 9, added NH_3 solution with vigorous stirring. 8 mL of TEOS was added to the solution and allowed the reaction for overnight with vigorous stirring. After the preparation of silica-coated magnetic nanoparticle were separated by using external magnetic field. The salinized magnetic nanoparticle were dried to obtain the powder [24].

2.4. Application of the proposed solid phase extraction method

The proposed solid phase extraction method was applied to three real water samples like tap water of analytical chemistry lab of this institute, River Kurram, Bannu and River Tochi, NWA for addition recovery. All the real water samples were passed through cellulose membrane filter having

0.45 µm pore size (Millipore) prior to solid phase extraction experiments to remove the solid suspended particles.

2.5. Batch adsorption studies

Batch adsorption studies were carried out in 50 mL of centrifuge tubes, which contain 10 µg mL^{-1} Cd (II) solutions at pH 7. The sample solutions were then added to another tubes contain 0.1 g of MNPs and SiMNPs and the solutions were allowed for 4 min under the influence of vortex having vortex speed of 10 × 40. After complete adsorption, MNPs and SiMNPs were separated by using external magnetic field and the liquid phase was separated using pipette. For quantitative recoveries of analyte, 2 mL of 1.0 M of HCl in acetone was added on the adsorbent. The solid phase was again subjected to vortex for 4 min and again separated using external magnetic field. Acetone in eluent was evaporated on water bath and 100 µL of eluent were injected to the nebulizer of the FAAS by using micro injection system for the measurement of concentration. Adsorption capacity of Cd (II) on MNPs and SiMNPs were calculated using the following equation [30] qþmG Z.

Fig. 1. Picture of MNPs to confirm its magnetic property.

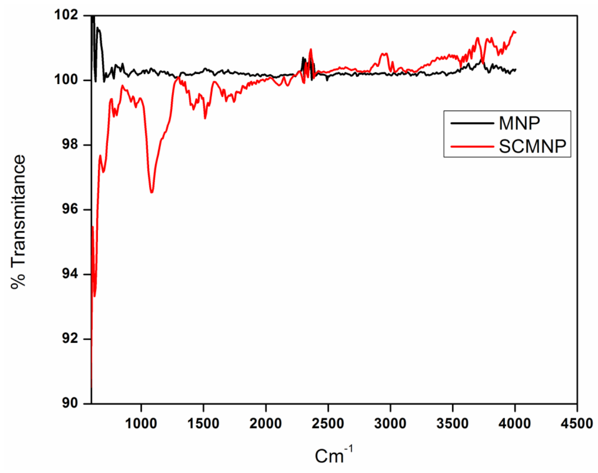


Fig. 2. FTIR spectra of MNPs and SiMNPs for surface functional group.

$$\text{Adsorption capacity } \left(q_e\right) = \left(C_o - C_e\right) V/m \tag{1}$$

where C_o and C_e are the initial and final concentration of Cd (II), q_t 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 g.

3. Result and discussion

3.1. Characterization of adsorbent

The adsorbents SiMNPs and MNPs were characterized by using FTIR, SEM, EDX and SAA. The strong absorption band in FTIR spectra (Fig. 2) at 1069.65 cm^{-1} correspond to Si-OH and Si-O-Si that confirms that the surface SiMNPs are covered by Si-OH functional group.

The physical nature and surface morphology of SiMNPs and MNPs can be viewed from SEM micrograph given in Fig. 3. More spherical and dispersed nature of SiMNPs (Fig. 3a and Fig. 3b) as compared to MNPs (Fig. 3c and Fig. 3d) can be seen from SEM micrograph. Thus the problem of self-aggregation of MNPs in aqueous solution can be minimize by coating Si-OH functional on the surface of MNPs.

The EDX mapping of SiMNPs and MNPs in Fig. 4 clearly shows high concentration of Si and Fe in SiMNPs (Fig. 4b) while high concentration of Fe is present in MNPs (Fig. 4a).

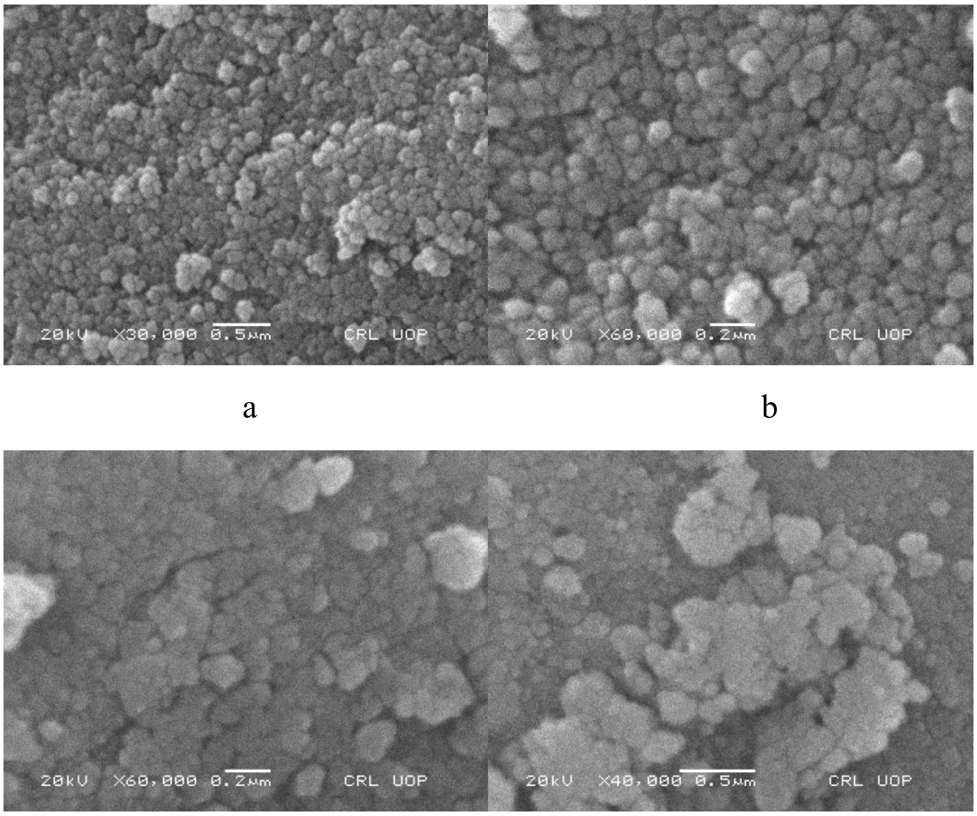
Surface area, pore size and pore volume of adsorbent were calculated by BET and BJH methods. According BET result the cumulative surface area of the MNPs and SiMNPs were determined as 80.18 mg^2/g and 81.35 respectively, while the BJH cumulative surface area of MNPs and SiMNPs were calculated as 104.8 m^2/g and 105.43 mg^2/g respectively. Also the average pore volume and pore size of MNPs are 0.21 ccg^{-1} and 44.23 A$^\circ$ respectively, while for SiMNPs the values are 0.27 ccg^{-1} and 46.41A$^\circ$ respectively.

3.2. Effect of pH

The effect of pH on % recovery of Cd (II) on MNPs and SiMNPs were investigated in the range of 2–9 as shown in Fig. 5. It can be concluded from Fig. 5 that% recoveries of Cd (II) increases with increase in pH and reach to its maximum value, which is 99±4%and 100±1 % on MNPs and SiMNPs, respectively. It can be explained that at lower pH, concentration of H$^+$ is high and compete with Cd (II) for the vacant sites on the adsorbent and decreases % recovery of Cd (II). The surface of adsorbent is neutral in the range of pH 6 to 8 and thus obtain quantitative % recovery of Cd (II) [31,32]. At higher pH metal hydroxide formation takes place which precipitated the metal-ion and decrease the % recoveries [31].

3.3. Effect of adsorbent dose

The effect of adsorbent dose on % recovery is an important parameter as it determines the maximum adsorption capacity of the adsorbent for constant adsorbate concentration. Therefore the solid phase extractions studies were carried out at different sorbent doses ranging from 0.02 g to 0.14 g as shown in Fig. 6. The % recovery result shows, that



a b

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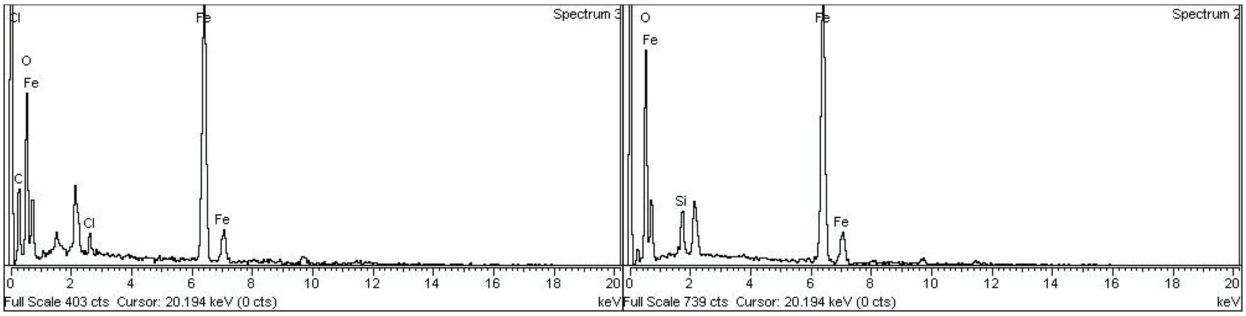
Fig. 3. SEM images of MNPs and SiMNPs for surface morphology.



a b

Fig. 4. EDX analysis for elemental analysis of MNPs and SiMNPs.

0.1 g is the smallest amount of adsorbent at which quantitative % recovery obtained. Therefore, 0.1 g was used in further optimization studies.

3.4. Effect of sample volume

In order to achieve highest preconcentration factor the solid phase extraction studies were conducted at different sample volume ranging from 5 mL to 50 mL (Fig. 7). Recovery results show that the proposed method can be successfully applied up to 40 mL of sample volume. Above 40 mL there is significant decrease in the percent recoveries of Cd (II). Therefore preconcentration factor of 20 can be achieved using 40 mL of sample and 2 mL of final volume.

3.5. Desorption studies

For quantitative percent recovery the proper type and concentration of eluting agent is of immense important. For this purpose mineral acids like HCl and HNO_3 were used

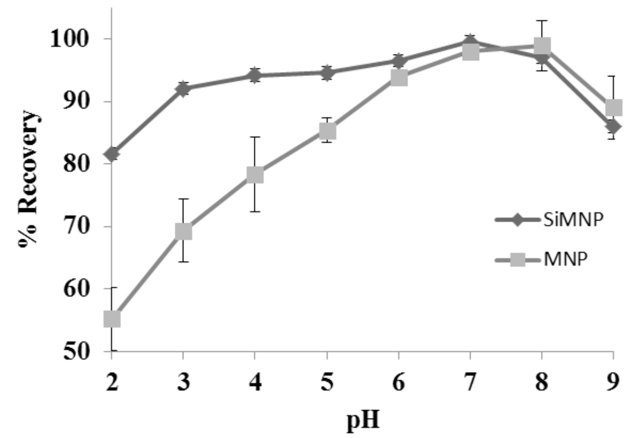


Fig. 5. Influence of pH on % recovery of Cd (II) using MNPs and SiMNPs (Volume of sample: 10 mL, amount of adsorbent: 0.1 g, final volume: 10 mL, *N* = 3).

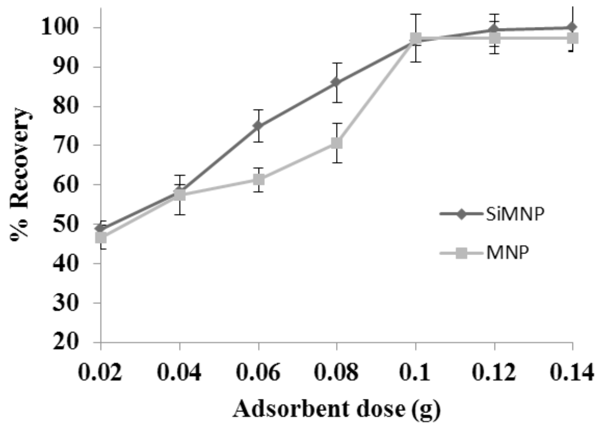


Fig. 6. Effect of adsorbent dose on % recovery of Cd (II) using MNPs and SiMNPs (pH: 7, Volume of sample: 10 mL, final volume: 10 mL, *N* = 3).

at different concentration like 0.25 mol L^{-1}, 0.5 mol L^{-1} and 1.00 mol L^{-1} both in water and acetone (Table 1). Recovery result obtained shows that 1 M of HCl is the best choice for complete desorption of Cd (II) from the surface of MNPs and SiMNPs to obtain quantitative recoveries.

After selecting proper type and concentration the volume of eluting agent was also optimized. Different volume (1–10 mL) of 1 mol L^{-1} of HCl in acetone was used for Cd (II) elution and the % recovery results are given in Fig. 8. Result shows that 2 mL of 1 mol L^{-1} HCl in acetone are enough for quantitative % recoveries.

3.6. Kinetic studies

To evaluate the kinetic studies, pseudo-first order, pseudo-second order kinetics, intraparticle diffusion and elovich

Table 1
Effect of type and concentration of eluent on % recovery of Cd (II) using MNPs and SiMNPs as adsorbents (*N* = 3).

Type and concentration of eluent	% Recovery	
	MNPs	SiMNPs
0.25 M HCl in water	45±6	34±4
0.5 M HCl in water	67±7	52±4
1 M HCl in water	86±5	65±3
0.25 M HNO_3 in water	37±4	32±4
0.5 M HNO_3 in water	54±4	47±7
1 M HNO_3 in water	83±3	59±6
0.25 M HCl in acetone	59±2	57±6
0.5 M HCl in acetone	89±6	80±5
1 M HCl in acetone	97±4	94±5
0.25 M HNO_3 in acetone	56±3	43±3
0.5 M HNO_3 in acetone	74±3	68±3
1 M HNO_3 in acetone	89±4	77±2

[a]Mean of three determinations ± standard deviation.

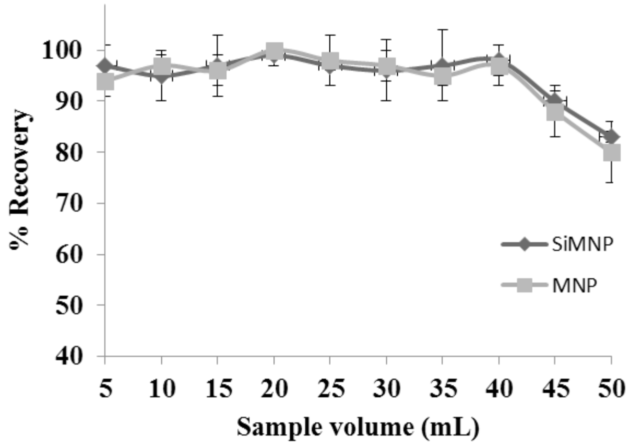


Fig. 7. Effect of volume of sample on % recovery of Cd (II) using MNPs and SiMNPs (pH: 7, Volume of eluent: 10 mL, amount of adsorbent: 0.1 g, N = 3).

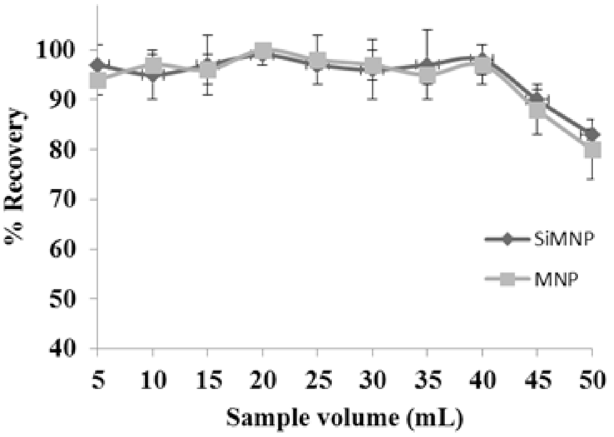


Fig. 8. Effect of volume of eluent on % recovery of Cd (II) using MNPs and SiMNPs (pH: 7, Volume of sample: 10 mL, amount of adsorbent: 0.1 g, *N* = 3).

kinetic model were employed to obtain useful information about adsorption efficiency of the adsorption of Cd (II) on SiMNPs and MNPs. For the pseudo-first order kinetics the equation is given as under [33].

$$log\ \left(q_e - q_t\right)\ =\ log\ q_e - \frac{k_1}{2.303}t \quad (2)$$

where q_t and q_e are the adsorption capacities at time t (min) and at equilibrium time respectively. 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 and are given in Table 2. The calculated adsorption capacities from pseudo-first order kinetics cannot coincide with experimental adsorption capacity. Therefore the adsorption of Cd (II) on SiMNPs and MNPs cannot follow pseudo-first order kinetics.

For the pseudo-second order kinetics following equation was used [33].

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_{2^{q_e 2}}} \quad (3)$$

where q_e and q_t are the sorption 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 and are given in Table 2. The calculated adsorption capacities from pseudo-first order kinetics are in close agreement with experimental adsorption capacities and the adsorption of Cd (II) on SiMNPs and MNPs follows pseudo-second order kinetics.

For the calculation of intra particle diffusion in the adsorption process of Cd (II) on MNPs and SiMNPs, the following equation used to described the intra particle diffusion model [34].

$$q_t = k_{\text{int}}\, t^{1/2} + c \quad (4)$$

where q_t is the sorption capacity at time t, K_{int} is the intraparticle diffusion rate constant, t is the time (min). The values of K_{int}, C and R^2 calculated from intraparticle diffusion model and are given in Table 2.

Table 2
Kinetic parameter for the adsorption of Cd (II) on MNPs and SiMNPs using different kinetic model

Kinetic model	Parameters	SiMNPs	MNPs
	$q_{e(exp)}$ (mg g^{-1})	22.39	21.812
Pseudo-first order model	k_1 (min^{-1})	0.062	0.0481
	q_e (mg g^{-1})	8.48	0.8077
	R^2	0.027	0.734
Pseudo-second order model	k_2 (min^{-1})	0.247	0.13
	q_e (mg g^{-1})	22.17	21.92
	R^2	0.9999	1
Intra particular diffusion model	k_{int} (min^{-1})	0.0129	0.147
	C	22.389	20.749
	R^2	0.0478	0.779
Elovich kinetic model	α (mg g^{-1} min^{-1})	6.91×10^{85}	5.6×10^{21}
	β (g mg^{-1})	8.69	2.522
	R^2	0.746	0.8615

The kinetics of chemisorption on heterogeneous surface is also calculated and explained by using elovich kinetic model which can be describe by the following equation [35].

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}lnt \quad (5)$$

where q_t is the sorption capacity in (mg g^{-1}) at time t, α and β represent the elovich coefficient. Where α is the initial rate of adsorption (mg g^{-1} min^{-1}), β (desorption constant) related to the extent of surface coverage. The value of α, β and R^2 for adsorption of Cd (II) on MNPs and SiMNPs were calculated from elovich kinetic model and are given in Table 2. High α values shows that initial rate of adsorption of Cd (II) on MNPs and SiMNPs is high.

3.7. Isotherm studies

Four adsorption isotherms Langmuir, Freundlich, Dubinin-Redushkviech (D-R), and Temkin were applied to adsorption of Cd (II) on SIMNP and MNP to express adsorption equilibrium.

Monolayer adsorption on homogenous surfaces can be best explained by using Langmuir adsorption isotherm and linear form of the Langmuir adsorption isotherm is given as under [36].

$$\frac{C_e}{q_e} = \frac{1}{k_L} + \frac{a_L}{k_L}C_e \quad (6)$$

where q_e is the adsorption capacity in (mg g^{-1}), C_e is the equilibrium concentration of the metal ion in (mg L^{-1}), a_L and k_L are Langmuir constant related to the adsorption energy and adsorbate – adsorbent binding force respectively. The values of these parameters, correlation co-efficient (r^2) and the theoretical monolayer adsorption capacity (Q^o) for the adsorption of Cd (II) on SiMNPs and MNPs were calculated and shown in the Table 3.

The linear and non-linear form of Freundlich adsorption isotherm can be expressed by using the following two equation [37]. Freundlich adsorption isotherm is use to explain metal adsorption on heterogeneous surfaces.

$$q_e = k_F C_e^{1/n} \quad (7)$$

$$log\ q_e =\ log\ k_F + \frac{1}{n}log\ C_e \quad (8)$$

where k_F is the relative adsorption capacity and $1/n$ indicates the intensity of adsorption process. The value of n, $1/n$, k_F and correlation coefficient (r^2) for the adsorption of Cd (II) and MNPs and SiMNPs were calculated and shown in Table 3.

The non-linear and linear forms of Temkin equation are given below [38].

$$q_e = \frac{RT}{b_T}ln\ (A_T C_e) \quad (9)$$

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (10)$$

Table 3
Comparison of the parameter of different isotherm model

Isotherm	Parameters	SiMNPs	MNPs
Freundlich	K_F (mg g^{-1})	481.947	354.8
	n	3.31	5.68
	$1/n$	0.302	0.1759
	R^2	0.8299	0.8228
Langmuir	a_L (Lmg^{-1})	5.33	1.06
	k_L (Lg^{-1})	3333.33	625
	Q^o (mgg^{-1})	625.33	588.51
	R^2	0.7776	0.9157
Temkin	A_T	186.20	1348.9
	B_T	91.025	53.431
	b_T	27.20	46.279
	R^2	0.6928	0.8099
D-R	q_m (mg g^{-1})	398.10	398.1
	k	1×10^{-8}	1×10^{-8}
	E (Kj mol^{-1})	7.142	0.877
	R^2	0.6486	0.8713

Table 4
Thermodynamic parameter for the adsorption of Cd (II) on MNPs and SiMNPs

	SiMNPs			MNPs		
Temperature, K	ΔG° J mol^{-1}	ΔH° J mol^{-1}	ΔS° J mol^{-1}	ΔG° J mol^{-1}	ΔH° J mol^{-1}	ΔS° J mol^{-1}
303	–16.0	28.24	0.148	–12.7	62.481	0.354
313	–17.25			–18.4		
323	–18.8			–20.9		
333	–19.5			–22.0		
343	–22.3			–24.6		
353	–23.0			–26.4		

where $B_T = \frac{RT}{b_t}$, T is the absolute temperature in Kelvin (K) and R is the universal gas constant (8.314 J mol^{-1} k^{-1}). The constant b_T is related to the heat of adsorption, A_T is another constant called equilibrium binding constant (L min^{-1}) related to the binding energy. The value of A_T and b_T for the adsorption of Cd (II) on SiMNPs and MNPs were calculated and given in Table 3.

D-R adsorption isotherm can be used distinguish between the chemical and physical adsorption process. The linear form of the equation is given as following [35].

$$\ln q_e = \ln q_m - K\in^2 \tag{11}$$

where q_e and q_m are the equilibrium and the maximum adsorption capacities Cd (II) on MNPs and SiMNPs respectively, K is a constant related to the adsorption energy (E), ∈ is the Polanyi potential which were describe by the following equation.

$$E = \frac{1}{\sqrt{2k}} \tag{12}$$

$$\in = RT\ ln \left(1 + \frac{1}{C_e}\right) \tag{13}$$

where C_e is the equilibrium concentration in mg L^{-1}, and T is the absolute temperature in Kelvin (K). The values of K and q_m, for the adsorption of Cd (II) on SiMNPs and MNPs were calculated shown in Table 2. E is a parameter that shows that whether the adsorption is chemical or physical process. When the value of E is in between 8 and 16 KJ mol^{-1}, then the adsorption is a chemical process and if the value is less than 8 KJ mol^{-1}, then the adsorption is a physical process. It can be seen in Table 3, that the value of E calculated from the model for the adsorption of Cd(II) on SiMNPs and MNPs 7.142 KJ mol^{-1} and 0.877 KJ mol^{-1} respectively is physical in nature.

3.8. Thermodynamic studies

For thermodynamic study the adsorption of Cd (II) on SiMNPs and MNPs were studied at different temperature. Various thermodynamic parameters like enthalpy (ΔH°), Gibbs free energy (ΔG°) and entropy (ΔS°) were calculated using the following equations [39].

$$K_D = \frac{q_e}{C_e} \tag{14}$$

$$\Delta G° = -RT \ln K_D \tag{15}$$

$$\Delta H° = R\frac{T_{2T_1}}{T_{2-T_1}} \ln \frac{K_2}{K_1} \tag{16}$$

$$\Delta S° = \frac{\Delta H_o - \Delta G_o}{T} \tag{17}$$

where K_D is the equilibrium constant, q_e and C_e are the equilibrium concentration of the metal ion on the adsorbent (mg L^{-1}) and the concentration of the metal ion in the solution (mg L^{-1}) respectively. It can be seen from Table 4, that the value of K_D increase with increase in temperature and also the value of ΔH° is positive which shows that the adsorption of Cd(II) on SiMNPs and MNPs is endothermic in nature. The positive values of ΔS° shows that these adsorption process is spontaneous in nature.

3.9. Matrix effect

The effects of different interfering ions which are coexisting with analyte metal in matrices of complex sample were studied and % recovery results are given in Table 5. It can be concluded from Table 5 that the presence of these coexisting cations has insignificant effect on % recovery of Cd (II) using MNPs and SiMNPs as adsorbents. Therefore it can be conclude that the proposed solid phase extraction is highly selective.

Table 5
Effect of coexisting ions on % recoveries of Cd (II) using SiMNPs and MNPs, pH: 7, amount of adsorbent: 0.1 g, concentration of Cd (II): 10 µg mL^{-1}, volume of sample solution: 10 mL (*N* = 3)

Interfering ions	Added as	Concentration, µg g^{-1}	Recovery, %	
			MNPs	SiMNPs
Na$^+$	NaCl	1000	96±2	95±4
K$^+$	KCl	1000	98±1	97±6
Ca^{++}	$Ca(NO_3)_2·4H_2O$	100	99±4	97±1
Mg^{++}	$Mg(NO_3)_2·6H_2O$	100	96±4	94±8
Al^{+++}	$Al(NO_3)_3·7H_20$	10	96±3	95±10
Zn^{++}	$Zn(NO_3)_2·6H_2O$	10	97±1	96±4
Fe^{++}	$Fe(NO_3)_2·6H_2O$	10	95±6	95±4
Cu^{++}	$Cu(NO_3)_2·6H_2O$	10	95±2	97±1
Ni^{++}	$Ni(NO_3)_2·6H_2O$	10	94±9	96±1
Mn^{++}	$Mn(NO_3)_2·6H_2O$	10	99±4	95±1
SO_4^-	Na_2SO_4	500	94±2	98±4
CO_3^-	Na_2CO_3	500	93±0	95±4
F$^-$	NaF	1000	100±5	96±1

[a]Mean of three determinations ± standard deviation.

Table 6
Analytical parameters of the method

Analytical parameter	MNPs	SiMNPs
Limit of detection (µg L^{-1})	0.31	0.30
Limit of quantification (µg L^{-1})	1.03	1.0
Preconcentration factor (PF)	20	20
Enhancement factor (EF)	19.9	19.7
Relative standard deviation (%)	4.6	5.2
Correlation coefficient (r^2)	0.998	0.999

3.10. Analytical performance of the method

All the analytical parameter like limit of detection (LOD), limit of quantification (LOQ), preconcentration factor (PF), enhancement factor (EF), relative standard deviation and correlation coefficient were calculated and given in Table 6. The values of LOD were calculated as the ratio of three times standard deviation of ten blank absorbance's to the slope of the regression equation while the values of LOQ were calculated as ten times standard deviation of ten blank absorbance's to the slope of the regression equation. The values of percent relative standard deviations were determines from five repeated determination having 5 µg g^{-1} concentrations. EF was calculated by using the ratio of the slops of the calibration curve drawn with and without the preconcentration step. PF was calculated as the ratio of the model solution to the final volume.

3.11. Application to the real sample

The proposed solid phase extraction method was applied for solid phase extraction of Cd(II) from tap water and river water samples and the % recovery results are given in Table 7. It can be concluded from Table 7 that all the % recovery results of Cd(II) are quantitative and the proposed solid phase extraction method can be successfully applied for real water samples.

The developed preconcentration method was compared with other preconcentration method in the literature regarding limit of detection as shown in the Table 8. It can be concluded that the method is either similar or superior as compared to other preconcentration method.

4. Conclusions

It can be concluded that:

1. Solid phase extraction method for the preconcentration of Cd(II) using MNPs and SiMNPs as adsorbents was developed.

Table 7
Addition recovery results for Cd (II) using the proposed solid phase extraction method (pH: 7, amount of adsorbent: 0.1 g, volume of sample: 15 mL, final volume: 2 mL (*N* = 3)

Sample	Added (µg mL^{-1})	MNPs	% Recovery	SiMNPs	% Recovery
		Found (µg mL^{-1})		Found (µg mL^{-1})	
Tap water	0	BDL	–	BDL	–
	10	9.4±0.8	94	9.6±0.7	96
	20	18.9±1.2	95	18.3±1.2	92
River Kurram, Bannu	0	0.5±0.04	–	0.6±0.04	–
	10	10.0±1.4	95	11.0±2.8	104
	20	20.8±0.9	102	20.0±1.9	97
River Tochi, NWA	0	0.8±0.02	–	0.68±0.02	–
	10	10.7±0.5	99	9.9±0.5	92
	20	20.4±1.4	98	20.7±1.4	100

[a]Mean ± standard deviation.

[b]BDL = Below of the detection limit.

Table 8
Comparison of the proposed solid phase extraction method with other pre-concentration methods

Method	LOD, µg L^{-1}	Samples	Ref.
Solid phase extraction	Cd: 0.15, Cu: 0.19, Pb: 2.03	Vegetable	[40]
Solid phase extraction	Cd: 0.6, Pb: 6.6	Water, Food	[41]
On- line separation	Cu: 1.0	Urine	[42]
Cloud point extraction	Cd: 1.4, Pb:2.6	Blood, Urine and Radiology waste	[43]
Solid phase extraction	Cd (II): 0.3	Water	This method

2. The method is highly sensitive with low values of limit of detections 0.31 µg L^{-1} and 0.30 µg L^{-1} MNPs and SiMNPs respectively.
3. Highly selective with no interfering effect from the matrix ion.
4. Reproducible with smaller values of percent relative standard deviations of 4.6 and 5.2 for MNPs and SiMNPs respectively.
5. Kinetic data fit to pseudo second order kinetics.
6. Thermodynamic data shows that the method is feasible in nature.
7. The method was successfully applied to environmental water samples like Tap water, River water for addition recoveries.

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