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Comparative solid phase extractions of Pb(II) from water samples using magnetic nanoparticles impregnated banana peels (MNPs-BP), magnetic nanoparticles (MNPs) and banana peels (BP)

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ABSTRACT

Solid phase extraction method for the preconcentration of Pb(II) from real water samples was developed by using magnetic nanoparticles impregnated banana peel, magnetic nanoparticle and banana peels as adsorbents. The adsorbents were characterized by using scanning electron microscope, energy dispersive X-ray and surface area analyzer. Parameters that influencing % recovery of Pb(II) such as solution pH, adsorbent dose, sample volume, concentration and volume of eluent and matrix effect were determined and optimized. Analytical parameters such as limit of detection, limit of quantification, preconcentration factor, enhancement factor and relative standard deviation were determined under optimized experimental condition. Kinetic data show that this adsorption study follow pseudo-second-order kinetics and the equilibrium data fit to Langmuir adsorption isotherm. The positive values of ΔH , ΔS and negative values of ΔG show that the adsorption process is endothermic, feasible and spontaneous in nature. The method was validated by applying the method to three real water samples with satisfied percent recoveries.

Keywords: Solid phase extraction; Magnetic nanoparticles; Impregnated

1. Introduction

Among all the heavy metals, lead is one of the most toxic heavy metal that accumulates in the living system and cause negative effects on the environment. Low level of lead cause anemia and high concentration of lead is responsible for dysfunction of kidneys, liver, cancer, damage to the central nervous system and high blood pressure [1,2]. Sources that discharge lead into the water streams include various kind of industries like acid metal plating and finishing, batteries manufacturing, tetraethyl lead manufacturing, ceramics and glass industries [3–6]. Therefore, accurate determination of lead in real environmental water samples is of immense importance [7]. Analytical techniques such as flame atomic absorption spectrometry and electrothermal atomic absorption spectrometry were largely used for quantification of lead in the environmental samples [8–11]. Due to low concentration of heavy metals in real water samples, it is difficult to directly determine its concentration using these analytical techniques. To overcome this problem, effective extraction and preconcentration methods are required [12].

In the literature, various treatment methods such as chemical precipitation, coagulation, membrane synthesis and extraction were employed for the preconcentration of heavy metal [13,14]. Liquid–liquid extraction techniques like dispersive liquid–liquid extraction [15], supramolecular solvent base liquid-phase extraction [16] and headspace liquid phase microextraction [17] have been extensively used by researchers in the recent past. Due to excessive discharge of organic compounds, significant interferences from matrix ions and low sensitivity in liquid–liquid extraction make it more expensive and also not environmental friendly. Therefore, solid phase extraction (SPE) method is more preferable over

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liquid–liquid extraction as it overcame the problems related with liquid–liquid extraction. In the last few decades, SPE methods attain rapid acceptance of the scientists. The SPE method is the alternative of the old classical liquid phase extraction having some advantages over it [14].

Various solid materials such as egg shell membrane [18,19], activated carbon, clay material and modified silica beads were used for the SPE of heavy metal [20]. Hemimiceles together with solid adsorbents were also used for SPE of heavy metals. The mixed hemimiceles has certain advantages in SPE method like high extraction rate, no clean up step, easy elution of the analyte and can be easily regenerate. However, if we use ordinary adsorbent having particle size in micrometer, then the SPE method is not effective. This limitation can be minimized by using nanomaterial as adsorbents for preconcentration of heavy metals in the environmental water samples [21].

The magnetic nanoparticles (MNPs) attract substantial interest of the scientific community due to its unique properties. Many nanometer-sized materials such as, carbon nanotubes [22], MNPs [23,24] and mesoporous material were used as SP adsorbents [25]. The size of the MNP falls in between 1 to 100 nm [26]. Due to smaller particle size, large surface area and magnetic property, the MNP can be used as an effective SP adsorbent for heavy metals in water samples. Magnetic SPE is an excellent method for the preconcentration of heavy metal from the aqueous solution [19,26].

In this SPE method, the adsorbent was produced by adsorbing ionic surfactant cetyltrimethylammonium bromide (CTAB) on MNPs and magnetic nanoparticle impregnated biosorbent banana peels (MNP-BP) and banana peels (BP) to produce mixed hemimiceles assemblies. The electrostatic attraction between head group of the surfactant and the oppositely charged oxide enable the formation of mixed hemimiceles [20]. This mixed hemimiceles were carried out for the SPE of Pb(II) from aqueous solution.

2. Experimental

2.1. Chemical

Ammonia solution (35%), hydrochloric acid (37%), methanol, sodium hydroxide, acetone, acetic acid, sodium acetate and cetyltrimethylammonium bromide were supplied by Riedel-de Haen Sigma-Aldrich (St. Louis, MO, USA). Lead(II) nitrate hexahydrate $Pb(NO_3)_2$, ferric chloride hexahydrate ($FeCl_3.6H_2O$), and ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), supplied by BDH laboratories, (BH15 ITD; UK). For pH adjustment, different combination of acids and salts (e.g., for pH 2–4, sodium dihydrogen phosphate/phosphoric acid; for pH 5.0–7.0, acetic acid and ammonium acetate; for pH 8.0, ammonia/ammonium chloride and for pH 9.0 and pH 10, sodium phosphate) were used.

2.2. Instruments

Flame atomic absorption spectrometer of Model A 300 (PerkinElmer, Norwalk, CT, USA) with specification: air–acetylene flame with 10 cm long-slot burner head and hollow cathode lamp was used as excitation source. Absorption measurement was carried out by injecting 100 μL of eluent to the nebulizer of the FAAS. The solid phase was separated by using an Nd magnet. Sonicator Model Ks-300 (KUM SUNG, Korea) was used for homogenous mixing of solutions. pH adjustment was carried out by using a pH electrode 422 WTW (Weilhmein, Germany).

SEM micrographs for surface morphology and EDX for elemental analysis of the adsorbent were investigated by using 30 kV SEM and EDX (JSM5910, JEOL, Japan). The surface area, pore volume and pore width of adsorbent were determined by BET-N_2 method using NOVA Quantachrome, USA.

2.3. Preparation of MNPs and MNP-BP

For preparation of MNPs and MNPs-BP, salts of Fe^{2+} and Fe^{3+} were mixed in 1:2 ratios in alkaline media for precipitation. For this purpose, 6.3 g of $FeCl_3.6H_2O$ and 4.2 g $FeSO_4.7H_2O$ were dissolved in 200 mL of distilled water with vigorous stirring under nitrogen atmosphere. The solution was kept at 80°C; black precipitate of MNPs was obtained when 20 mL of 25% ammonia solution was added. The Fe_3O_4 obtained was washed twice with distilled water, dried in oven at 100°C [19].

$$Fe_3O_4.\ 7H_2O + 2FeCl_3.6H_2O + 8NH_4OH \rightarrow Fe_3O_4 + 6NH_4Cl + (NH_4)_2SO_4 + 17H_2O$$

BP were collected from juice shops, washed with distilled water and dried it in sunlight. The dried BP were grinded in grinder and passed through sieve to obtain uniform particle size of 355 μm. Powder BP were washed several times with distilled water and ethanol in order to completely remove the dust particles. For the impregnation of MNPs on BP, 5 g of BP was added to the solution of MNPs at 80°C for 120 min under vigorous stirring. The resultant MNPs-BP was filtered, washed twice with distilled water and dried in oven at 100°C. The MNPs-BP obtained was checked for its magnetic property with magnetic rod shown in Fig. 1 [27,28].

$$Fe_3O_4 + BP \rightarrow Fe_3O_4\text{-}BP$$

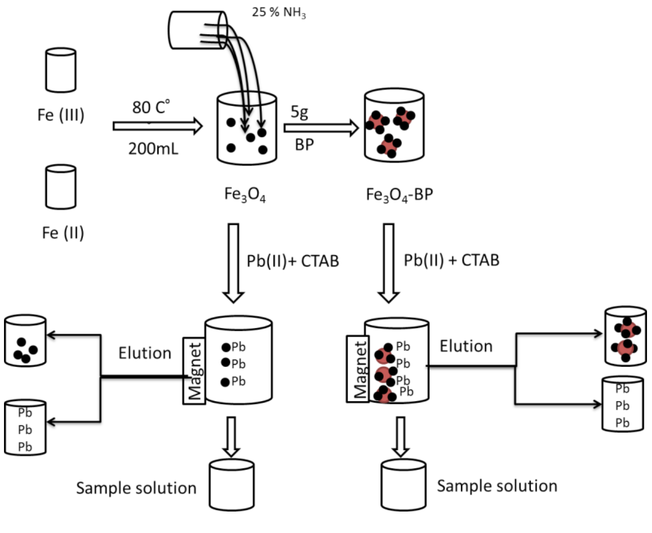

Fig. 1. Graphical representation of the developed solid phase extraction method.

2.4. Application of the proposed SPE method to real sample

The proposed SPE method was applied to three real water samples like dam water (Baran Dam, Bannu), river water (River Tochi, NWA) and waste water (Board bazar canal, Peshawar). All the suspended particles were removed by using 0.45 μm size membrane supplied by (Millipore Corporation, Bedford, MA, USA).

2.5. Batch adsorption studies

In the batch adsorption studies, 0.1 g of adsorbents and 0.6 g of surfactant (CTAB) was taken in 50 mL of centrifuge tube and added 5 mL of buffer solution to completely soak the adsorbent. Sample solution (20 μg mL^{-1}) 20 mL of Pb(II) were added to the flask and allow the adsorption reaction for 5 min under the influence of vortex having (40 × 100 rpm) vortex speed. Solid phase was separated by using Nd magnetic and the liquid phase was transferred to another tube carefully. To the solid phase, 2 mL of 2 M HCl in acetone was added to elute the adsorbed Pb(II) from the surface of adsorbents. After 5 min of sonication, the eluent was separated again by Nd magnet and 100 μL was injected to the nebulizer of the FAAS by using microinjection system for absorption measurement. Following equation was used to calculate adsorption capacity:

$$\text{Adsorption capacity } \left(q_e\right) = C_0 - C_e)V/M \quad (1)$$

where C_0 and C_e are the initial and final concentration of Pb(II), q_t is the adsorption capacity in mg g^{-1}, V is the volume of Pb(II) in mL and m is the mass of adsorbent in grams.

3. Results and discussion

3.1. Characterization of adsorbents

Surface morphology can be best examined by studying SEM micrograph of the adsorbents (Fig. 2). SEM micrograph of BP, MNPs-BP and MNPs can be seen from Fig. 2. BP shows porous surface morphology with pore size of 0.11 μm (Fig. 2(c)). Surface morphology of MNPs-BP confirms the successful impregnation of BP with MNPs (Fig. 2(b)) and MNPs uniformly present the particle size, that is, 110and 100 nm; or 0.11 and 0.1 μm (Fig. 2(a)).

Elemental analysis of MNPs, MNPs-BP and BP can be determined by analyzing the EDX mapping (shown in Fig. 3). High concentration of Fe in MNPs (Fig. 3(a)) and MNPs-BP (Fig. 3(b)) confirm the impregnation of MNPs on the surface of BP. Fe concentration is almost negligible in the case of BP (Fig. 3(c)).

Brunauer, Emmett, Teller (BET) and Barrett, Joyner, Hallenda (BJH) surface area, pore volume and pore size of MNPs, MNPs-BP and BP were determined by using N_2 adsorption/desorption methods and the results are given in Table 1. Increase in BET surface area of BP occur from 28.92 to 49.71 m^2 g^{-1} after modification with MNPs. Pore volume and pore size also increases from 0.11 to 0.14 ccg^{-1} and 139.43 to 142.23 Å, respectively.

3.2. Effect of pH on adsorption

Preconcentration of Pb(II) was studied over pH range of 3–9 using MNPs-BP, MNPs and BP and % recovery results are shown in Fig. 4. It can be concluded from the Fig. 4 that % recovery of Pb(II) increases as pH of the solution increases from 3 to 7. There is a significant decrease in % recovery of Pb(II) above pH 7. It can be explained that as pH of the solution increases, the electrostatic attraction between Pb(II) and negatively charged surface of the adsorbent also increases and thus increase % recovery. Another explanation is that

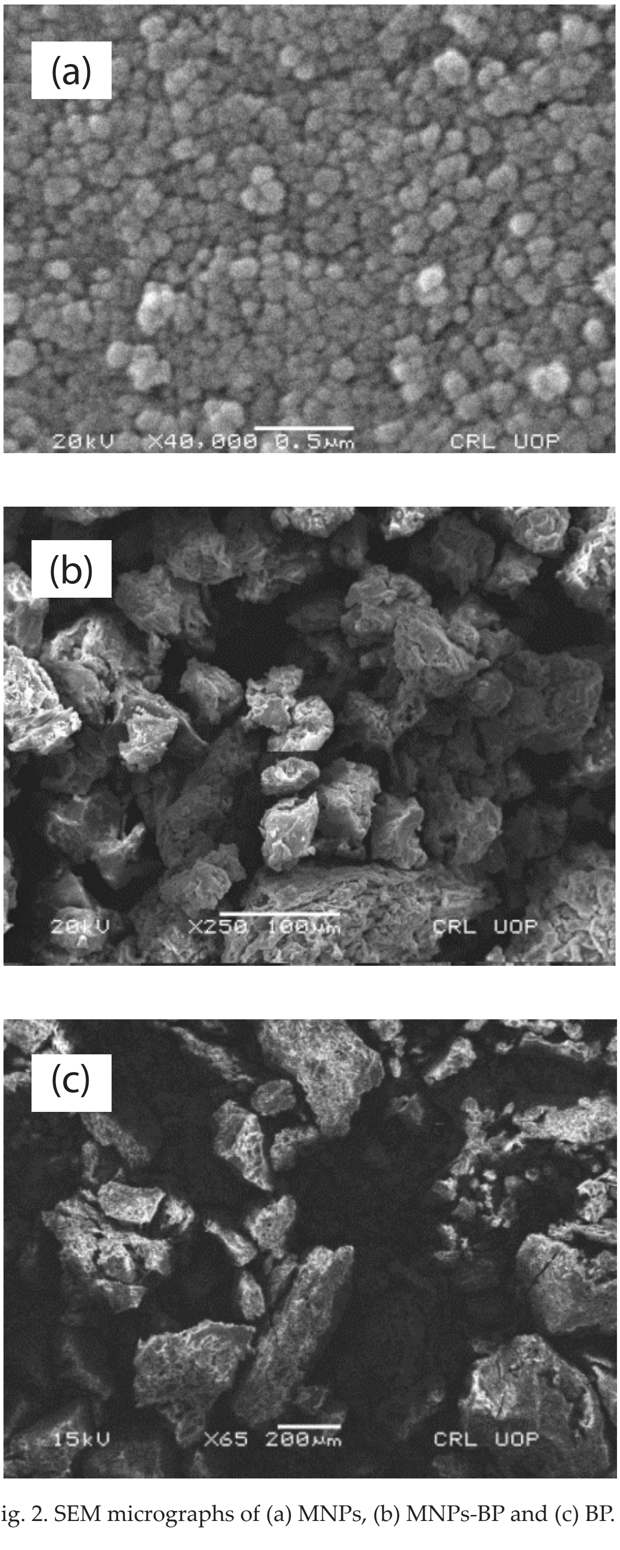

Fig. 2. SEM micrographs of (a) MNPs, (b) MNPs-BP and (c) BP.

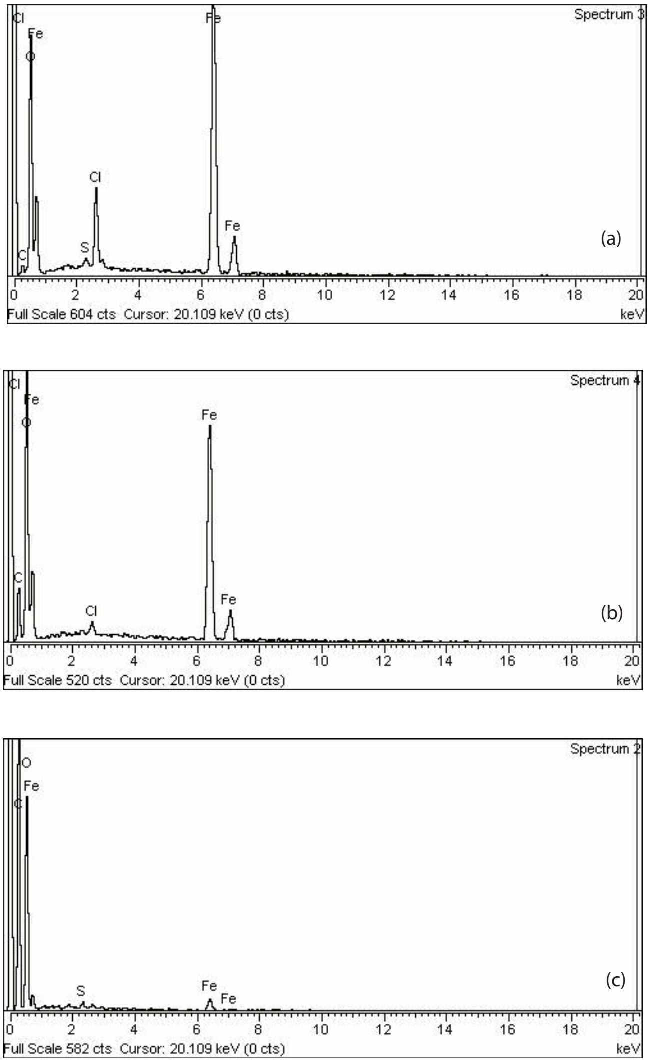

Fig. 3. EDX patterns of (a) MNPs, (b) MNPs-BP and (c) BP.

Table 1
Surface area, pore volume and pore size of MNPs-BP, MNPs and BP by BET and BJH methods

Sample	Method	Surface area ($m^2 g^{-1}$)	Pore size (ccg^{-1})	Pore volume, (Å)
MNPs	BET	80.14	0.21	44.32
	BJH	104.9		
MNPs-BP	BET	49.71	0.14	142.23
	BJH	58.67		
BP	BET	28.92	0.11	139.43
	BJH	41.53		

at low pH, the H^+ ion concentrations is high and occupies most of the vacant sites of the adsorbent and thus decrease the % recovery of Pb(II). Above pH 7 metal hydroxide formation takes place that also decrease the % recovery of Pb(II). Therefore, pH 7 was the optimum pH which was maintain in other optimization studies.

3.3. Effect of adsorbent dose

The effect of adsorbent dose is an important parameter because it determines the adsorption capacity of the adsorbent for constant initial adsorbate concentration. Therefore, the SPE studies were carried out at different adsorbent doses of 20–140 mg as shown in Fig. 5. It can be concluded from Fig. 5 that % recovery of the Pb(II) increase rapidly with increase in adsorbent dose of MNPs, MNPs-BP and BP. After the critical dose 100 mg, the % recovery of Pb(II) reached to a constant value. Therefore, 100 mg was the optimum adsorbent dose that was maintained in further preconcentration studies.

3.4. Effect of sample volume

In order to obtain highest preconcentration factor (PF), the proposed SPE studies were carried out at different

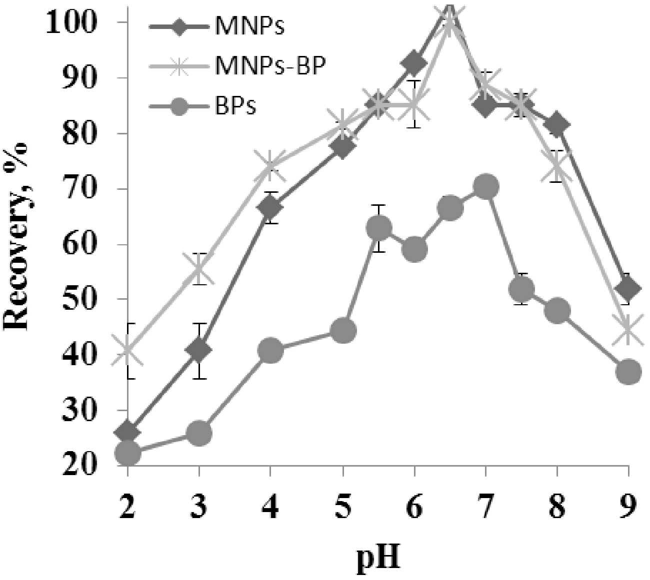

Fig. 4. Effect of pH on % recovery of Pb(II) using MNPs-BP, MNPs-BP and BP.

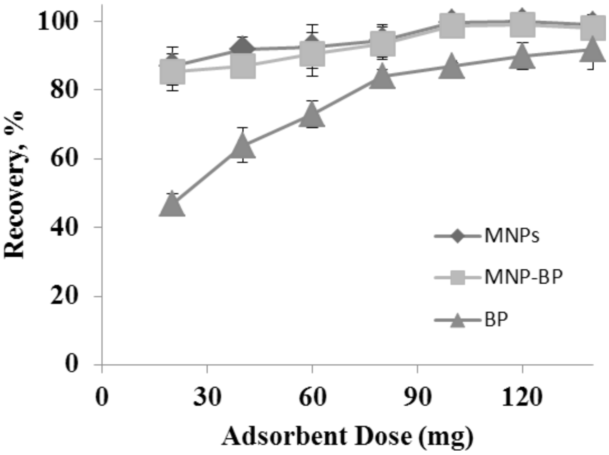

Fig. 5. Effect of adsorbent dose on % recovery of Pb(II) using MNPs-BP, MNPs and BP.

sample volume ranging from 5 to 50 mL (Fig. 6). Quantitative % recoveries were obtained up to 40 mL in case of MNPs-BP and MNPs, while in the case of BP, quantitative % recovery was achieved up to 15 mL. Therefore, PFs 20 can be achieved in case of MNPs-BP and MNPs and 15 in the case of BP.

3.5. Desorption studies

For complete desorption of Pb(II) from the surface of MNPs-BP, MNPs and BP, mineral acids such as HCl and HNO_3 were used as eluents in the concentration range of 1–3 mol L^{-1} (Table 2). A recovery result shows that 2 mol L^{-1} of HCl was the best choice to obtain quantitative % recovery.

After selecting type and concentration of eluent, volume optimization is of enormous importance. Therefore, desorption studies were carried out at different volume ranging from 1 to 8 mL of 2 mol L^{-1} HCl (Fig. 7). % recovery results show that 2 mL of 2 mol L^{-1} HCl is enough to obtain quantitative % recoveries in case of MNPs-BP and MNPs, while in the case of BP quantitative % recoveries were obtained with 1 mL of 2 mol L^{-1} HCl.

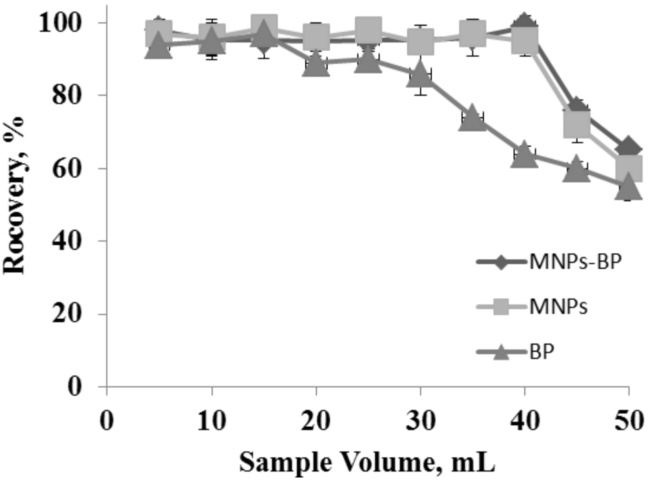

Fig. 6. Effect of sample volume on % recovery of Pb(II) using MNPs-BP, MNPs and BP.

Table 2
Effect of type and concentration of eluent on percent recovery of Pb(II) using MNPs, MNPs-BP and BP as adsorbents

Type and concentration of Eluent	% Recovery		
	MNPs	MNPs-BP	BP
1 M HCl	83 ± 3	59 ± 1	85 ± 2
2 M HCl	94 ± 1	97 ± 5	97 ± 2
3 M HCl	91 ± 4	94 ± 3	91 ± 4
1 M HNO_3	79 ± 2	81 ± 1	86 ± 4
2 M HNO_3	83 ± 1	90 ± 4	91 ± 1
3 M HNO_3	84 ± 1	86 ± 3	84 ± 3

Note: pH: 7, amount of adsorbents: 0.1 g, volume of sample solution: 10 mL (*N* = 3).
[a]Mean ± standard deviation.

3.6. Adsorption kinetics

For adsorption kinetics, two kinetic models such as pseudo-first-order kinetics and pseudo-second-order kinetics were employed. Pseudo-first-order kinetics can be represented by the following equation [29]:

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

where q_e and q_t are the amount of adsorbate adsorbed (mg g^{-1}) at equilibrium time and at contact time *t* (min), respectively, and k_1 is the rate constant (min^{-1}) for pseudo-first-order kinetics of the adsorption process. The values of q_e and k_1 were calculated from the slop and intercept of the plot of log ($q_e - q_t$) vs. *t*, respectively. The values of $k_{1,}$ correlation coefficient and q_e (experimental and calculated) are summarized in Table 3. The experimental q_e values, $q_{e(\text{exp})}$ did not agree with calculated values, $q_{e(\text{cal})}$, obtained from the linear plots. It shows that the adsorption of Pb(II) on MNPs-BP, MNPs-BP and BP cannot follow pseudo–second-order kinetics.

The pseudo-second-order kinetics model can be expressed by the following equation [30]:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_{e^2}} \qquad (3)$$

where k_2 is the rate constant of pseudo-second-order kinetics (g $\text{mg}^{-1}\text{min}^{-1}$). The values of q_e and k_2 were determined from the intercept and slop and presented in Table 3. The linear plot shows a good agreement between experimental and calculated q_e values (Table 3). Beside this the corresponding correlation coefficient values are also high that shows that the adsorption of Pb(II) on MNPs-BP, MNPs-BP and BP follow pseudo-second-order kinetics. It means that pseudo-second-order kinetics parameter obtained could be used to determine rate constant, equilibrium sorption capacity, percentage removal of Pb(II) and initial rate of adsorption. Since this adsorption process follow pseudo-second-order

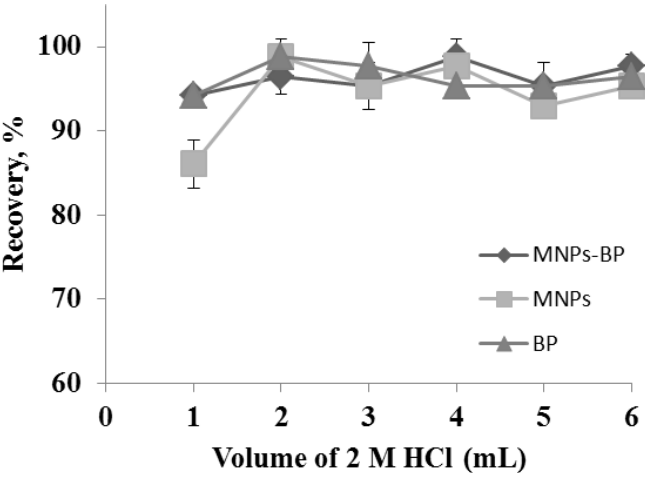

Fig. 7. Effect of volume of eluent on % recovery of Pb(II) using MNPs-BP, MNPs and BP.

kinetics, thus the SPE of Pb(II) on MNPs-BP, MNPs and BP was controlled by chemisorption [31,32].

3.7. Isotherm studies

For isotherm studies, Langmuir and Freundlich adsorption isotherms were employed. Monolayer adsorption on homogenous surfaces can be best explained by using Langmuir adsorption isotherm. The linear form of Langmuir adsorption can be expressed by using the following equation [33]:

$$\frac{C_e}{q_e} = \frac{1}{k_\mathrm{L}} + \frac{a_\mathrm{L}}{k_\mathrm{L}} C_e \tag{4}$$

where C_e is the equilibrium concentration of the metal ion in mg L^{-1}, q_e is the adsorption capacity in mg g^{-1}, a_L and k_L are Langmuir constants related to the adsorption energy and adsorbate–adsorbent binding force, respectively. The values of these parameters, correlation coefficient (R^2) and the theoretical monolayer adsorption capacity ($Q°$) for the adsorption of Pb(II) on MNPs-BP, MNPs and BP was calculated and shown in Table 4.

The linear and non-linear forms of Freundlich adsorption isotherm can be expressed by using the following two equations [34]:

$$q_e = k_\mathrm{F} C_e^{\,1/n} \tag{5}$$

$$\log q_e = \log k_\mathrm{F} + \frac{1}{n} \log C_e \tag{6}$$

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 Pb(II) on MNPs-BP, MNPs and BP was calculated and given in Table 4.

3.8. Thermodynamic studies

For thermodynamic studies, the SPE of Pb(II) on MNPs-BP, MNPs and BPs was carried out at different temperatures ranging from 303 to 353 K as shown in Fig. 8. Various thermodynamic parameters such as enthalpy ($\Delta H°$), Gibbs free energy ($\Delta G°$) and entropy ($\Delta S°$) were calculated using the following equations [35,36]:

$$K_D = \frac{q_e}{C_e} \tag{7}$$

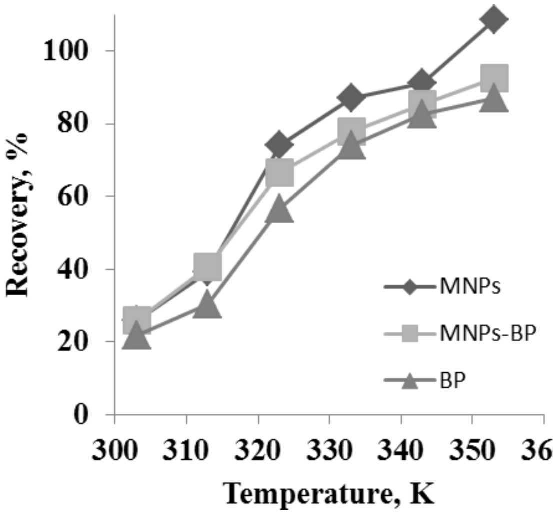

Fig. 8. Effect of temperature on % recovery of Pb(II) using MNPs-BP, MNPs and BPs.

Table 3
Kinetic parameters for the adsorption of Pb(II) using MNPs-BP, MNPs and BP as adsorbents

Adsorbent	Experimental q_e (mg g^{-1})	Kinetic models					
		Pseudo-first order			Pseudo-second order		
		K_1 (min^{-1})	q_e (mg g^{-1})	R^2	$K_{2\,\mathrm{min}}{}^{-1}$	q_e (mg g^{-1})	R^2
MNPs-BP	0.2	0.467	0.138	0.904	5.76	0.217	0.995
MNPs	0.2	0.048	0.133	0.854	5.55	0.216	0.992
BP	0.12	0.218	0.75	0.887	7.46	0.126	0.976

Table 4
Comparison of different isotherm parameters

Adsorbent	Isotherm model							
	Freundlich				Langmuir			
	K_F (mg g^{-1})	n	$1/n$	R^2	K_L (L g^{-1})	a_L (L mg^{-1})	$Q°$ (mg g^{-1})	R^2
MNPs	1.87	3.7	0.3	0.967	769	1.00	0.769	0.988
MNPs-BP	2.84	2.2	0.4	0.867	5,000	0.25	20.000	0.985
BP	0.25	2.6	0.3	0.869	833	0.249	3.332	0.831

$$\Delta G° = -RT \ln K_D \tag{8}$$

$$\Delta H° = R\frac{T_2T_1}{T_2 - T_1}\ln\frac{K_2}{K_1} \tag{9}$$

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} \tag{10}$$

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. Positive values of ΔH and ΔS in Table 5 shows that the adsorption of Pb(II) on MNPs-BP, MNPs and BP is endothermic and spontaneous in nature.

3.9. Matrix effect

The selectivity of the method can be investigated by studying the effect of different ions, which are coexisting with analyte ions especially in the samples of complex matrix nature. For this purpose, the SPE studies of Pb(II) on MNPs-BP, MNPs and BP were carried out in the presence of different interfering ions. % recovery results are given in Table 6 and shows that the effect of these ions on % recoveries of Pb(II) is insignificant. The study shows that the SPE of Pb(II) on MNPs, MNPs-BP and BP is highly selective.

Table 5
Thermodynamic parameter for the adsorption of Pb(II) on MNPs-BP, MNPs and BP

Temperature, K	MNPs-BP			MNPs			BP		
	Δ G, KJ mol^{-1}	Δ H, KJ mol^{-1}	Δ S, KJ mol^{-1}	Δ G, KJ mol^{-1}	Δ H, KJ mol^{-1}	Δ S, KJ mol^{-1}	Δ G, KJ mol^{-1}	Δ H, KJ mol^{-1}	Δ S, KJ mol^{-1}
303	−8.963	59.23	0.331	−8.985	54.54	0.243	−8.381	23.11	0.132
313	−1.102			−10.843			−9.841		
323	−1.424			−15.176			−13.082		
333	−1.623			−18.017			−15.646		
343	−1.813			−19.854			−17.591		
353	−2.094			…			−19.099		

Table 6
Matrix effect (pH: 7, amount of adsorbent: 0.1 g, volume of sample: 15 mL, final volume: 2 mL ($N = 3$)

Interfering ions	Added as	Concentration, μg mL^{-1}	% Recovery		
			MNPs-BP	MNPs	BP
Na^{1+}	NaCl	2,500	99 ± 1[a]	100 ± 5	99 ± 4
K^{1+}	KCl	2,500	100 ± 4	96 ± 1	95 ± 3
Ca^{++}	$Ca(NO_3)_2.4H_2O$	500	97 ± 1	93 ± 0	95 ± 4
Mg^{++}	$Mg(NO_3)_2.6H_2O$	500	99 ± 4	93 ± 1	96 ± 1
Al^{+++}	$Al(NO_3)_3.7H_20$	100	98 ± 4	94 ± 5	94 ± 5
Cd^{++}	$Cd(NO_3)_2.6H_2O$	100	97 ± 8	97 ± 8	100 ± 5
Zn^{++}	$Zn(NO_3)_{2.}6H_2O$	100	102 ± 9	94 ± 2	94 ± 2
Fe^{++}	$Fe(NO_3)_{2.}6H_2O$	100	93 ± 1	93 ± 1	96 ± 2
Cu^{++}	$Cu(NO_3)_{2.}6H_2O$	5	98 ± 2	98 ± 2	98 ± 2
Ni^{++}	$Ni(NO_3)_{2.}6H_2O$	5	94 ± 2	94 ± 2	94 ± 8
Mn^{++}	$Mn(NO_3)_{2.}6H_2O$	5	95 ± 1	93 ± 8	93 ± 4
SO_4^{--}	Na_2SO_4	500	93 ± 7	100 ± 4	100 ± 3
CO_3^{--}	Na_2CO_3	500	98 ± 2	93 ± 6	93 ± 4
F^-	NaF	100	94 ± 1	96 ± 8	96 ± 7

[a]Mean of three determinations ± standard deviation.

3.10. Analytical parameters of the method

Various analytical parameters such as limit of detection (LOD), limit of quantification, PF, enhancement factor (EF) and relative standard deviation (RSD) of the developed method were calculated by using the same procedure as given by Khan et al. [36] and the values are given in Table 7. It can be concluded from the values that the method is highly sensitive, efficient and reproducible.

3.11. Validation of the proposed SPE method

For validation and addition recovery of Pb(II), the proposed SPE method was applied to three real water sample like river water (River Tochi, NWA), dam water (Baran Dam, Bannu) and waste water (Board bazar canal, Peshawer) samples and the % recovery results are given in Table 8. It can be concluded from Table 8 that all the % recovery results of Pb(II) are quantitative and the proposed SPE method can be successfully applied for real water samples.

For the comparison of the developed SPE with other preconcentration method, analytical parameter such as LOD and PF were selected. The comparisons result in Table 9 shows that the method is either similar or superior as compared with the other preconcentration methods.

4. Conclusions

SPE method for the preconcentration of Pb(II) using MNPs-BP, MNPs and BP as adsorbents was developed. Low values of LODs shows that the method is highly sensitive. The developed method is highly selective with no interfering effect from the matrix ion. Smaller values of percent RSD show that

Table 7
Analytical parameters of the proposed solid phase extraction method

Analytical parameters	MNPs	MNPs-BP	BP
Limit of detection (μg L^{-1})	0.576	0.519	0.876
Limit of quantification (μg L^{-1})	2.921	1.730	2.921
Preconcentration factor (PF)	20	20	15
Enhancement factor (EF)	17.1	39.65	12.1
Relative standard deviation (%)	6.1	4.02	4.6
Correlation coefficient (r^2)	0.966	0.957	0.876

Table 8
Addition recovery results for Pb(II) using the proposed solid phase extraction method

Adsorbent	Sample	μg Added	μg Found	% Recovery
MNPs-BP	River water	0.000	UDL	…
		10.000	9.195	92 ± 0
		16.666	13.937	86 ± 6
	Dam water	0.000	UDL	…
		10.000	9.162	92 ± 0
		16.666	13.703	83 ± 5
	Waste water	0.000	UDL	…
		10.000	9.162	94 ± 0
		16.666	14.370	87 ± 1
MNPs	River	3.333	UDL	…
		10.000	8.897	89 ± 3
		16.666	14.270	88 ± 0
	Dam water	0.000	3.114	…
		10.000	8.997	90 ± 2
		16.666	14.403	86 ± 1
	Waste water	0.000	UDL	…
		10.000	8.617	87 ± 2
		16.666	14.303	86 ± 1
BP	River water	0.000	UDL	…
		10.000	9.642	96
		16.000	15.876	99
	Dam water	0.000	UDL	
		10.000	9.189	92
		16.000	15.765	99
	Waste water	0.000	UDL	…
		10.000	9.542	95
		16.000	15.654	98

Note: pH: 7, amount of adsorbent: 0.1 g, volume of sample: 15 mL, final volume: 2 mL (*N* = 3).
[a]Mean ± standard deviation.
[b]BDL, below of the detection limit.

Table 9
Comparison of the developed solid phase extraction method with other preconcentration methods

Method	Analysis	Detection limit, μg L^{-1}	Sample	References
CPE[a]	FAAS[e]	Cd: 1.4, Pb:2.6	Environment	[37]
SPE[b]	FAAS	Pb(II): 3.9, Co(II): 2.9	Environment	[38]
DLLME[c]	XFS[f]	Pb(II): 2.6, Co(II): 0.7	Water	[39]
IL-DLLME[d]	PZAAS[g]	Pb(II): 9.5	Environment	[40]
SPE	FAAS	Cd: 0.6, Pb: 6.6	Water and Food	[41]
SPE	FAAS	Pb: 0.523 to 0.876	Water	This work

[a]Cloud point extraction; [b]Solid phase extraction; [c]Dispersive liquid–liquid extraction; [d]Ionic liquids–dispersive liquid–liquid microextraction. [e]Flame atomic absorption spectrometry; [f]X-ray florescence spectrometry; [g]Poler Zeeman atomic absorption spectrometry.

the method is highly reproducible. Kinetic data show that this adsorption studies follows pseudo-second-order kinetics. Equilibrium data fit to Langmuir adsorption isotherm. Thermodynamic data show that the method is endothermic and feasible in nature. For addition recovery, the method was applied to real water samples with satisfied % recoveries.

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