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Synthesis of a novel ion-imprinted polyaniline/hyper-cross-linked polystyrene nanocomposite for selective removal of lead(II) ions from aqueous solutions

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ABSTRACT

This study concerns on the preparation of a novel Pb(II) ion-imprinted polymer (Pb(II)-IIP) based on the hyper-cross-linked polystyrene as porous support via precipitation polymerization of aniline, as functional monomers,and ammonium per sulfate, as the initiator. The prepared materials were characterized by Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), liquid nitrogen physisorption analysis, energy dispersive X-ray spectroscopy (EDX), and transmission electron microscopy (TEM) techniques. The potential of the prepared adsorbent for removing lead ions from water solutions was investigated in batch extraction experiments. The effect of three main variables affecting the adsorption process including pH, agitation time, and adsorbent dosage were screened. It is found that, under the optimum experimental conditions, the kinetics of the process follows pseudo-second-order reaction. Langmuir adsorption model described well the isotherm of the process. The results showed that the investigated adsorbent bears a good capacity and selectivity towards lead ions. Relatively fast adsorption kinetic was a further advantage of the developed adsorbent. It was shown that the adsorbent is stable and can be reused in 6 adsorption-desorption cycles.

Keywords: Ion imprinted polymers; Porous polymer; Lead ions; Adsorption

1. Introduction

Heavy metals contamination of water, soil and air are serious environmental problem and attracted much attention of research groups to develop new and efficient methods for monitoring and controlling these sources of environmental menace. Among the heavy metal pollutants, lead has been recognized as one of the severely toxic metals resulting from mining, metallurgical engineering, lead-acid battery manufacturing, textile industries, electroplating, printing, ceramic, explosive manufacturing and glass industries [1]. It is well known that lead containing piping material is the principal source of contamination [2]. The presence of higher concentrations of Pb(II) causes various severe environment and human problems [3]. It is well known that Pb(II) ion are non-degradable with long half-life and tends to accumulate in the living organisms, thus its removal is of great concern in water treatment and environmental management.

The potential of natural and synthetic adsorbents for removal of heavy metals from water solutions is well documented [4,5]. This potential has been widely considered for refinement of lead decontaminated water samples by using carbon-based nanomaterials [6,7], cellulose nanocomposite [8], membranes [9,10], clays [11,12], zeolites [13], modified silica [14,15] and modified polymer materials [16,17].

Although the known advantages of adsorption technique for decontamination of heavy metals from water sources,

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the application of this method is limited in some extent by its low selective attitude and the interferences generated by other co-extracted species with the target analyte [18]. To overcome this limitation, the development of molecular imprinted polymers (MIPs) has been proposed [19]. Imprinting in framework of organic polymers make access to highly selective synthetic receptors with template recognition sites designed for a particular group of target chemical species [20]. High adsorption capacity and stability are further characteristics of these group of materials which highlighted them among the investigated adsorbents [21].

Synthesized sorbents in the presence of an ion, as a template, generate ionic imprinted polymers (IIPs) offer all the benefits derived from molecularly imprinted polymers (MIPs) with a high capacity towards recognizing ions [22]. There are some recent literature reports on the preparation of IIPs for recognition of Pb(II) ions. Among these are polyamine grafted on the surface of silica gel [23], imprinted polymer in nano-TiO_2 matrix [24], copolymer of the vinylpyridine (VP) and ethyleneglycoldimethacrylate [25,26], chitosan on ordered mesoporous silica SBA-15 [27] polyethylene glycol dimethacrylate-dithizone nanobeads [28], ion-imprinted silica sorbent functionalized with chelating N-donor atoms [29], magnetic ion-imprinted polymer [21,30], 8-hydroxyquinoline-grafted gelatin with different types of functional groups [31] and ion-imprinted silica adsorbent modified diffusive gradients [32].

To the best of our knowledge, there is no previous literature report on the use of polyaniline (PANI) in hyper-cross-linked polystyrene (HPS) for the preparation of Pb(II) ion-imprinted polymeric nanocomposite. Such material can be considered as potential adsorbent for decontamination of aqueous solutions from lead ions.

This present paper describes the preparation and characterization of a new Pb(II) ion-imprinted polymer (Pb(II)-IIP-PANI/HPS) based on the hyper-cross-linked polystyrene as porous support via precipitation polymerization of aniline monomers in the presence of ammonium per sulfate. The applicability of the prepared adsorbents has been examined for removal of lead ions from water solutions.

2. Experimental

2.1. Materials

The hyper-cross-linked polystyrene as Macronet-MN270 was obtained from Purolite Int., UK. and washed with water and acetone twice. Aniline monomer (Merck), ammonium persulfate (Fluka), nitrate salts of lead, copper, cadmium and nickel (Sigma-Aldrich) and solvents (Merck) were used as received. The stock solution of metals (1000 mg L^{-1}) were prepared by dissolving the appropriate amounts of the corresponding nitrates in deionized water and acidified with nitric acid (0.01 mol L^{-1}). Working solutions were prepared daily by proper dilution of the stock solution with deionized water. Deionized water (18.2 MΩ cm) was used throughout performing the experiments.

2.2. Apparatus and instruments

IR spectra (400–4000 cm^{-1}) were recorded on a FT-IR Brucker-Vector 22 spectrophotometer (Bruker, Germany) in KBr/Nujol mull. DSC analysis was carried out by using a Mettler Toledo DSC 821e system at a heating rate of 10°C per minute under N_2 gas atmosphere over a temperature range 25–600°C. Belsorp mini II, (BEL Japan Inc.) was employed to investigate the nitrogen adsorption–desorption isotherms at 77K. Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were used to calculate the surface area and pore size distribution of the prepared nanocomposite. JEOL JSM-7100 scanning electron microscopy (SEM) and energy dispersive X-ray analyses (EDX) were utilized to investigate the morphology and elemental composition of the product. Transmission electron microscopy (TEM) images were taken on a Philips EM208 electron spectroscopic microscope at 100 kV. A Varian Spectra AA 220 atomic absorption spectrophotometer (AAS) was used for the analysis of the metal ions. Deionized water was produced by an M–UV–3^+Zolalan (Iran) water purification system. A Metrohm pH meter (model 780) equipped with a combined glass electrode was used for all pH adjustments.

2.3. Preparation of Pb(II)-IIP-PANI/HPS

In a typical procedure, HPS (0.05 g), aniline monomer (2 mL) and ethanol (10 mL) were placed in the round-bottom flask. The mixture was stirred overnight, at room temperature. Afterwards, the reaction mixture was filtered off and washed with ethanol and deionized water. To the filtrate in a round bottom flask was added 10 mL of water, 10 mL of ethanol and 0.1 mmol of lead nitrate), ethanol (10 mL) and $Pb(NO_3)_2$ (0.1 mmol). This mixture was stirred for 2 h. The polymerization was started by addition of ammonium persulfate solution (0.5 g in 5 mL deionized water). The resulted mixture gently stirred overnight at room temperature. The product was recovered via vacuum filtration and was washed with deionized water and ethanol. Then it was washed three times with stirring in 10 mL HNO_3 (0.1 mol L^{-1}). Finally, the final product (Pb(II)-IIP-PANI/HPS), was recovered by filtration, washed with deionized water and ethanol.

2.4. Metal uptake batch experiment

A 30 mg portion of the sorbent (IIP-PANI/HPS) was added into 10 mL of aqueous solutions containing 10 mg L^{-1} of Pb(II) adjusted at pH 6.0.The pH adjustment was performed by using HNO_3 and NaOH solutions (0.1 mol L^{-1}). The mixture was magnetically stirred at room temperature for 2 h. After filtration, the concentration of Pb(II) in the aqueous phase was analyzed by flame atomic absorption spectroscopy. The percentage of the adsorbed lead ions was calculated using Eq. (1):

$$\text{Removal}(\%) = \frac{(C_0 - C_e)}{C_0} 100 \tag{1}$$

where C_0 and C_e are initial and equilibrium concentrations of metal ions (mg L^{-1}), respectively. The optimal conditions for the absorption of lead ions by the prepared sorbent (IIP) was assessed by investigation the effect of aqueous phase pH, adsorbent dose and contact period on the adsorption efficiency.

2.5. Kinetics of the process

Kinetics of the adsorption process were screened by stirring the mixtures of 30 mg of IIP-PANI/HPS with 10 mL of lead ion aqueous solution (10 mg L^{-1}) adjusted at pH 6.0, in the range 25–180 min and the amount of lead ions remained (C_t) in the aqueous solutions was analyzed by FAAS.

The adsorption capacity (q) at time t was calculated according to Eq. (2):

$$q_t = \frac{\left(C_0 - C_t\right)}{m} \tag{2}$$

where V (mL) and m (g) are the volume of the solution and the weight of absorbent, respectively.

2.6. Adsorption isotherm

Different dosages of IIP were added into each conical flask directly. 10 mL of Pb(II) aqueous solution with concentration (C_0) of 10 mg L^{-1} adjusted at pH 6 were then added into each conical flask. The suspension was agitated at room temperature. After the adsorption reached equilibrium, the concentration (C_e) of lead ion in the aqueous solution was analyzed by atomic absorption spectrophotometer.

2.7. Selectivity experiments

To examine the adsorption selectivity of IIP-PANI/HPS, 10 mL of a mixture of Pb(II), Cu(II), Ni(II), and Cd(II) ions (10 mg L^{-1}, each) were contacted 30 mg of the sorbent, for 2 h,under the optimized experimental conditions. After phase disengagement by filtration, the concentration of residual metal ions in the solution was analyzed by FAAS. The distribution coefficient K_d (mL g^{-1}), selectivity coefficient k, and the relative selectivity coefficient k' were defined as:

$$K_d = \frac{\left(C_0 - C_e\right)V}{C_e m} \tag{3}$$

$$k = \frac{K_d^{Pb^{2+}}}{K_d^{M^{n+}}} \tag{4}$$

$$k' = \frac{k_{IIP}}{k_{NIP}} \tag{5}$$

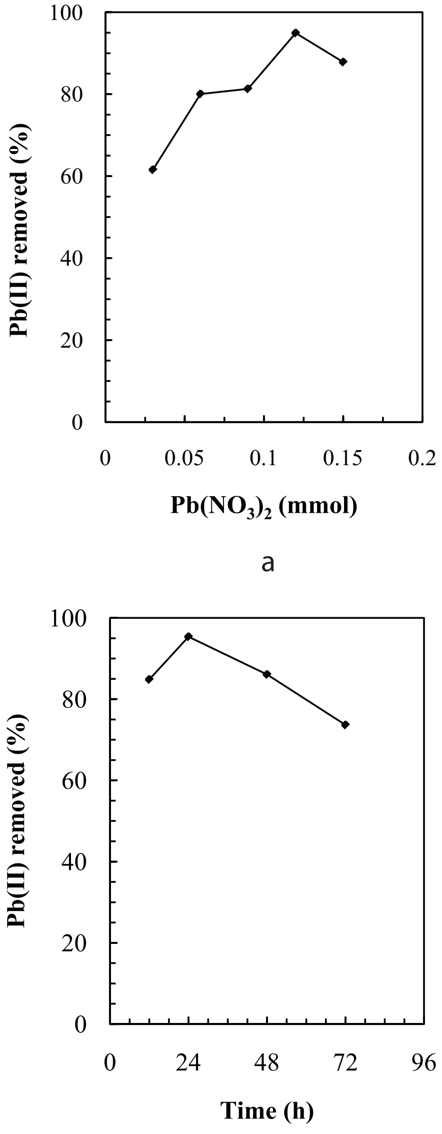
In these equations V (mL) is the volume of initial solution of metal ions and m (g) is the adsorbent dose. k_{IIP} and k_{NIP} are selectivity coefficients of the ion imprinted and non-imprinted polymer, respectively.

3. Results and discussion

3.1. Preparation of lead ion imprinted polyaniline supported by hyper-cross-linked polystyrene (IIP-PANI/HPS)

In this study, hyper-cross-linked polystyrene (HPS) as porous support was subjected to treat with an appropriate concentration of functional monomer, aniline, in the presence of ammonium persulfate (APS) to start polymerization in ethanol aqueous solution. Polyaniline in this method was synthesized by chemical oxidation of aniline by APS [33].

The reaction was further optimized for the influences of template amount and polymerization time. This optimization was followed by adsorption efficiency of the prepared ion imprinted nanocomposite towards Pb(II) ions from water solutions. To this end, the preparation was carried out by mixing 0.05 g of HPS with four different amount of lead(II) nitrate (0.03, 0.06, 0.09, 0.12 and 0.15 mmol) in the presence of aniline and ammonium persulfate at room temperature. It was seen that the adsorption capacity of the prepared adsorbent towards Pb(II) increased with increasing the template ion concentration up to 0.12 mmol (Fig. 1a). Beyond this value the adsorption efficiency was decreased.



a

b

Fig. 1. Effect of different reaction parameters on the removal percentage of IIP-PANI/HPS sorbent: lead(II) nitrate amount (a); polymerization time (b). The results are average of three independent experiments with a standard deviation (1σ*n*–1) ≤ 2.5%.

The effect of the reaction period (6, 12, 24, 48, and 72 h) also was examined, while all the other parameters were kept constant. The adsorption of lead ions was decreased for the reaction period more than 24 h (Fig. 1b). These observations strongly confirmed that an increase in the amount of template or reaction time would enable the bulk formation and reduce the surface area and the accessibility of active surface sites for efficient adsorption of the pollutant.

3.2. Characterization of IIP-PANI/HPS

Characterization of the prepared IIP-PANI/HPS was realized by different techniques including FT-IR spectroscopy, liquid nitrogen physisorption, Differential scanning calorimetry (DSC), Energy-dispersive X-ray spectroscopy (EDX) and Transmission electron microscopy (TEM) analysis. The FT-IR spectra of the HPS, prepared nanocomposite before leaching the Pb(II) (Pb@PANI/HPS), IIP-PANI/HPS and for that non-imprinted polymer (NIP) nanocomposite were investigated in order to get detailed information about the chemical functional moieties on the adsorbent (Fig. 2).

Comparison of the FT-IR spectra showed, although all the vibrations of the hyper-cross-linked polystyrene and polyaniline were remained, the significant changes appeared for many characteristic bands. As instance, N–H group characteristic absorption band shifted from 3389 cm^{-1} for IIP-PANI/HPS to 3421 cm^{-1} for Pb@PANI/HPS nanocomposite, and obviously was become broad. Also, the characteristic feature of quinoid ring modes at 1633 cm^{-1} shifted to lower wavenumber (1604 cm^{-1}) and absorption peak of C–N at 1417 cm^{-1} shifted to 1384 cm^{-1}. The results were in agreement with those PANI has been loaded successfully on the HPS. It was also seen that the amine groups in polyaniline has been coordinated with Pb(II) simultaneity from the observed changes in the spectra.

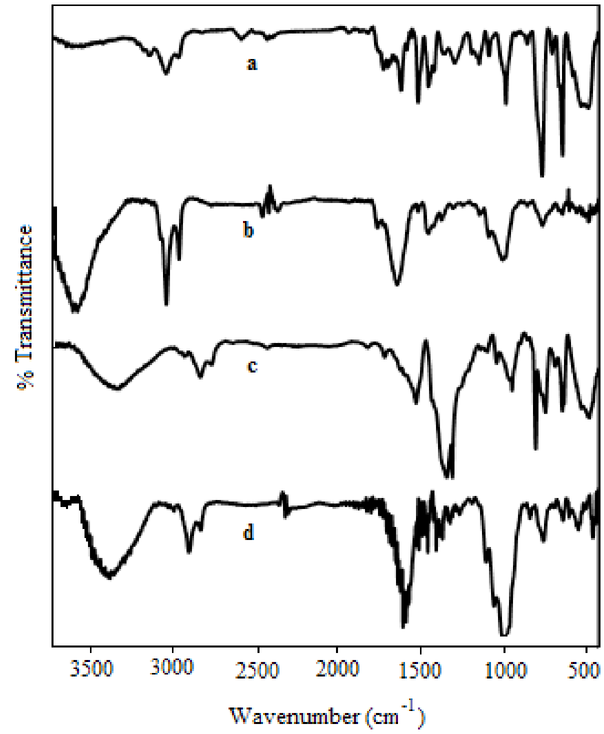


Fig. 2. FT-IR spectra of HPS (a); NIP (b); Pb(II)@PANI/HPS (c); IIP-PANI/HPS (d).

DSC technique was applied for investigation of the thermal behavior of the prepared ion imprinted nanocomposite and deducing the changes in its aggregation structures during the polymerization and imprinting process. The thermal behavior of the matrix phase (HPS) was also taken, for comparison (Fig. 3a). For Pb@PANI/HPS composite three distinguishable transitions appeared at 36.15, 360.46, and 431.06°C (Fig. 3b). The DSC profile of IIP-PANI/HPS revealed transitions at 104.83, 329.28 and 449.27°C (Fig. 3c). The last peak can be attributed to the transition temperature of HPS matrix. Analysis of the DSC curves of ion imprinted nanocomposite (IIP-PANI/HPS) and that of Pb@PANI/HPS did not show a significant changes in their transition temperature.

Table 1 summarizes the calculated Brunauer–Emmet–Teller (BET) surface area and total pore volume of HPS, Pb(II)@PANI/HPS and IIP-PANI/HPS. The results revealed that after polymerization the surface area and the total pore volume were decreased. This was attributed to the deposition occurred on the surface and within the pores of the porous matrix. It is noteworthy that a little increase of surface area and pore volume of the IIP signifies the presence of the cavities after leaching of the metal ions.

Furthermore, from the EDX analysis (Fig. 4a), C, O and Pb are the main elements of Pb(II)@PANI/HPS, while C, O and N are the main elements of IIP-PANI/HPS (Fig. 4b). Apparently, the C and N elements come from polyaniline and hyper cross linked polystyrene. The EDX analysis indicated that the lead ion was only present in the Pb(II)@PANI/HPS composite and it was removed after leaching process.

The morphology of the prepared materials was investigated by transmission electron microscopy (TEM) technique. The TEM image of the Pb(II)@PANI/HPS revealed the existence of lead nanoblocks inside the nanocomposite with the average diameter of ~20 nm (Fig. 5a). It was consistent with the results of TEM analysis, indicating that the lead template was well removed from IIP-PANI/HPS (Fig. 5b).

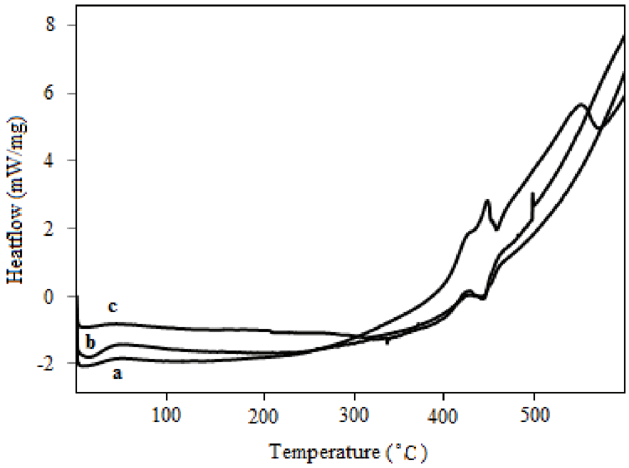


Fig. 3. Differentiating scanning calorimetric analysis (DSC) of HPS (a); Pb(II)@PANI/HPS (b); IIP-PANI/HPS (c).

Table 1
The porosity of HPS, Pb(II)@PANI/HPS and Pb(II)-IIP-PANI/HPS

Sample	a_s ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)
HPS	1537	1.2
Pb(II)@PANI/HPS	1130	0.71
IIP-PANI/HPS	1175	0.84

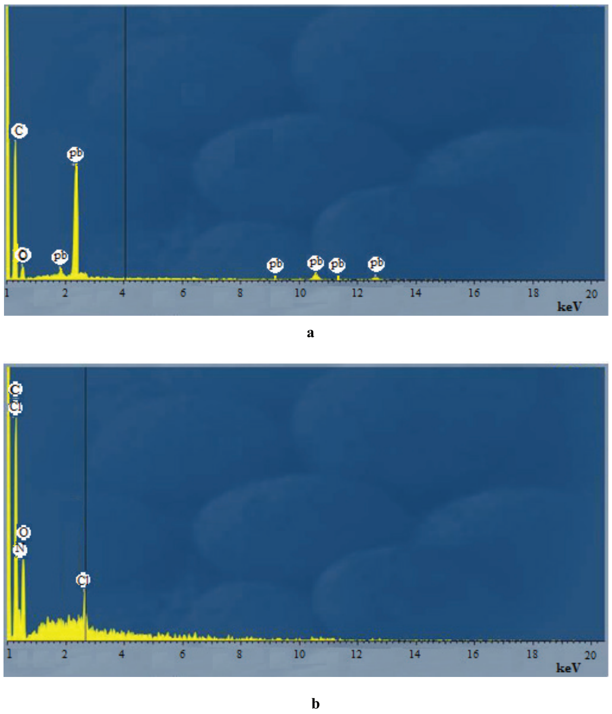


Fig. 4. EDX analysis of Pb(II)@PANI/HPS (a); IIP-PANI/HPS (b).

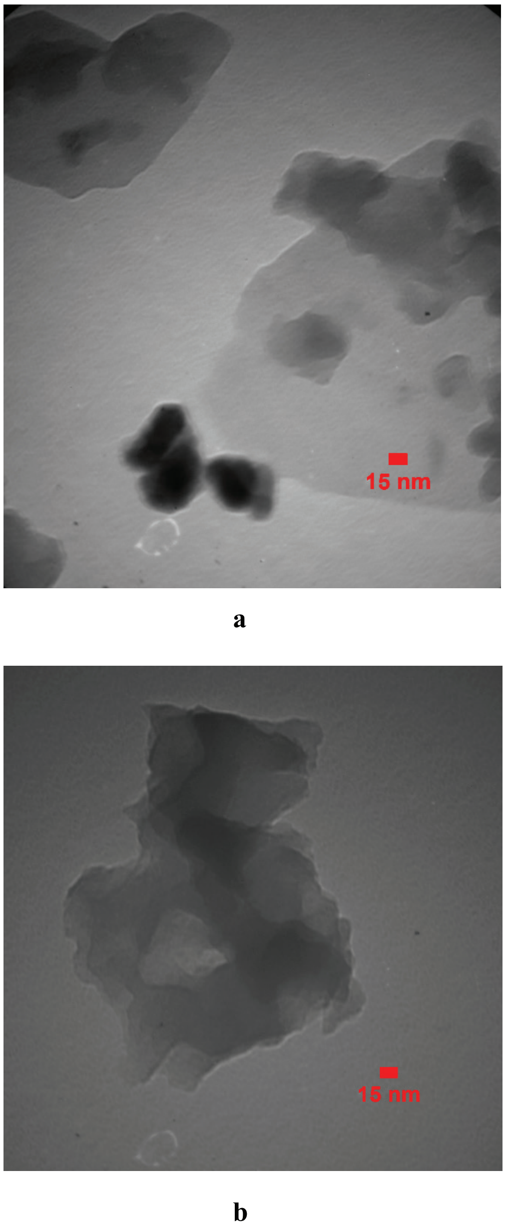


Fig. 5. TEM images of Pb(II)@PANI/HPS (a) IIP-PANI/HPS (b).

3.3 Adsorption properties of IIP-PANI/HPS

3.3.1. Effect of the pH of the solution

The effect of hydrogen ion concentration on the adsorption efficiency of the prepared IIP-PANI/HPS was surveyed by varying the aqueous phase pH in the range 1–6 (Fig. 6a). The metal uptake decreased in acidic aqueous solutions, while the binding of Pb(II) ions was enhanced by increasing the aqueous phase pH. As expected, due to the existence of amine functional group in the imprinted sorbent, the removal percentage is highly dependent on the pH of the solution. This pH dependency can be attributed to the protonation of functional groups and hydrolysis of the metal ions which is in agreement with the negligible amounts of lead ions adsorption at the lower pH values.

3.3.2. Effect of adsorbent dose

In order to choose a proper adsorbent dose, a series of adsorption experiments of lead ions (10 mg L^{-1}) from aqueous phase adjusted at pH 6 were performed by using different amount of IIP-PANI/HPS in the range 0.005–0.06 g (Fig. 6b). The percent removal of lead ions is sharply increased with adsorbent dose. This dependency can be described by the accessibility to more binding sites (amino groups) by increasing the amount of the adsorbent. A quantitative removal of the lead ions was observed by using ≥ 0.03 g of the adsorbent. Therefore, 0.03 g of the adsorbent was selected as optimal amount.

3.3.3. Time dependency of the adsorption process

The effect of the agitation time on the uptake efficiency of lead ion from aqueous solutions by the imprinted adsorbent IIP-PANI/HPS was monitored by performing a series

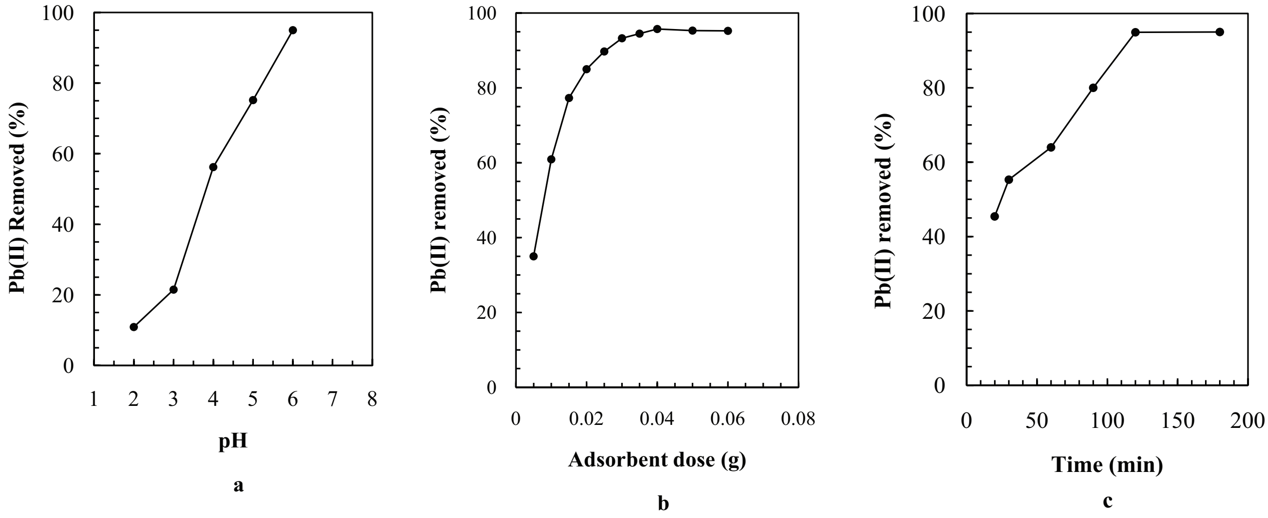


Fig. 6. Variation of the removed Pb(II) (10 mg L^{-1}) from aqueous solutions by IIP-PANI/HPS adsorbent as a function of (a) pH of the aqueous solution; (b) adsorbent dose; (c) contact time. The results are average of three independent experiments with a standard deviation (1σ*n*–1) ≤3.1%.

of experiments at different contact time in the range 20–180 min, while other parameters were kept at the optimum conditions. The results are shown in Fig. 6c.

3.3.4. Adsorption isotherms

In order to describe the distribution of Pb(II) ions between liquid and solid phase at equilibrium condition, the isotherm models such as, Langmuir, Freundlich and Dubinin–Radushkevich (D–R) were used to fit the experimental data and exploring of the mechanism of adsorption. A mathematically representation of Langmuir model is given in Eq. (6):

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \tag{6}$$

q_e (mg g^{-1}) and q_{max} (mg g^{-1}) are the amount of metal ions adsorbed at equilibrium and the capacity of adsorbent, respectively. b (L mg^{-1}) is a constant related to energy of the adsorption process. The dimensionless separation factor R_L is used to predict of the affinity of adsorbate and adsorbent:

$$R_L = \frac{1}{1+bC_0} \tag{7}$$

The corresponding equation for Freundlich model is:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{8}$$

In this equation K_F (mg g^{-1}) (mg L^{-1})^n and n (a dimensionless parameter) are the constants. These parameters represent adsorption capacity and adsorption intensity, respectively.

The mathematical description of Dubinine-Radushkevich (D–R) model is given below:

$$\ln q_e = lnq_{\max} - \beta\varepsilon^2 \tag{9}$$

$$E = \frac{1}{\sqrt{2\beta}} \tag{10}$$

where β (mol^2 kJ^{-2}) is the activity coefficient related to the mean sorption energy and ε signifies the Polanyi potential.

Table 2 contains the evaluated parameters calculated by applying Langmuir, Freundlich and D–R isotherms on the experimental data. The evaluated R^2 values allows considering that the Langmuir equation gives the best fit to the adsorption. The results show that the investigated adsorption system is favorable for Pb(II) and adsorption belonged

Table 2
Evaluated parameters by applying Langmuir, Freundlich and D–R models on the experimental results.

Isotherm	Parameter	IIP-PANI/HPS
Langmuir	R^2	0.996
	q_{max} (mg g^{-1})	16.7
	b (L mg^{-1})	0.75
	R_L	0.12
Freundlich	R^2	0.991
	k_F ((mg g^{-1}) (mg L^{-1})^n)	7.26
	n	2.72
	$1/n$	0.37
D-R	R^2	0.988
	q_{max} (mg g^{-1})	0.00054
	β (mol^2 kJ^{-2})	2.98 10^{-3}
	E (kJ mol^{-1})	12.95

to a uniformly and single molecular layer adsorption on the active sites of the adsorbent.

The resulting values calculated by the Freundlich model, $1/n < 1$, revealed the fact that a favorable nonlinear adsorption taken place on adsorbent surface.

Furthermore, the values of E (kJ mol^{-1}) from D-R model ($8 < E < 16$) indicate that chemical sorption is occurred. These data are in agreement with the effect of pH and contact time on the Pb(II) ions adsorption.

3.3.5. Equilibrium sorption time

The rate of adsorption is one of the important characteristics which describe the efficiency of an adsorption process. The obtained kinetic adsorption data of Pb(II) ions, two different kinetic models i.e. pseudo-first-order and pseudo-second-order equations were assessed.

The pseudo-first-order equation is given by:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303} t \qquad (11)$$

In this equation k_1(min^{-1}), q_e and q_t (mg g^{-1}) are the rate constant, the adsorption capacity at equilibrium "*e*" and time "*t*", respectively.

The pseudo-second-order equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (12)$$

here k_2 (mg g^{-1} min^{-1}) is pseudo-second-order rate constant. The evaluated kinetics constants are given in Table 3.

A comparison of the evaluated correlation coefficients for pseudo-second-order model (R^2 = 0.974) and pseudo-first-order (R^2 = 0.952) models allows concluding that the kinetics of the adsorption obeyed from pseudo-second-order kinetic model. In addition close value of the calculated adsorption capacity (q_e) predicted by the latter model with that obtained experimentally (q_e (exp)) reconfirm this conclusion. This model suggests that the chemical adsorption may be the rate-limiting step and the adsorption behavior might involve the valence forces through sharing electrons between the lead ions and adsorbents.

3.3.6. Selectivity study

The selectivity behavior of the investigated adsorbent towards Pb(II) ions was examined by performing its adsorption in the presence of some associated ions including Cu(II), Ni(II) and Cd(II) from their mixtures, using Pb(II)-IIP-PANI/HPS and NIP as adsorbents (Fig. 7 and Table 4).

As shown in Table 4, the distribution ratio (K_d) of IIP for Pb(II) is significantly greater than other ions. The selectivity coefficient (*k*) values for IIP of Pb(II)/Cu(II), Pb(II)/Ni(II) and Pb(II)/Cd(II), were found to be 15.51, 1.78 and 4.39, respectively. It is interesting to note that, NIP has low *k* value due to the absence of the particular binding sites in a predetermined orientation and special size of the cavity. It is well known that, in IIP, the selectivity is affected by this fact that the cavities created after removal of the imprint ion were complementary of the template in shape, size and coordination geometries.

Table 3
Kinetic parameters obtained by applying the pseudo first order and pseudo second order models on the experimental results

q_e(exp)	Pseudo-first-order			Pseudo-second-order		
	k_1	q_e	R^2	k_2	q_e	R^2
6.33	0.0161	4.59	0.952	0.0059	6.62	0.974

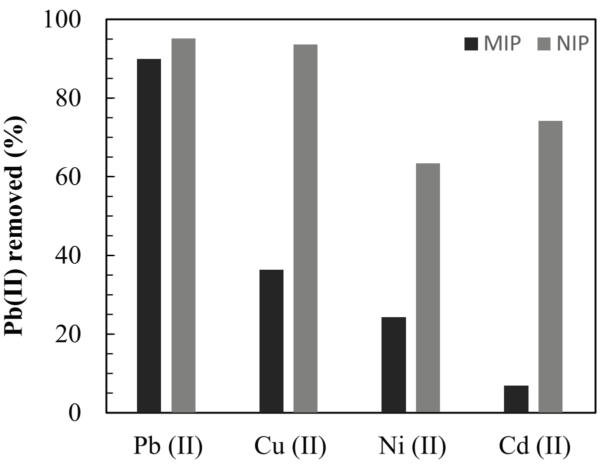


Fig. 7. The results of competitive adsorption experiments of Pb(II), Cu(II), Ni(II) and Cd(II) by IIP-PANI/HPS and NIP. Experimental conditions: adsorbent 30 mg; aqueous phase pH 6.0; initial metal ions concentration 10.0 mg L^{-1}, adsorption time 2.0 h; at room temperature. The results are average of three independent experiments with a standard deviation (1σ*n*–1) ≤3.0%.

Table 4
Competitive sorption of Pb(II) and metal ions on ion-imprinted polymer (IIP-PANI/HPS) and non-imprinted polymer (NIP)

Metal ion	IIP-PANI/HPS		NIP		*k′*
	K_d	*k*	K_d	*k*	
Pb(II)	2935.90	–	6333.33	–	–
Cu(II)	189.22	15.52	4794.87	1.32	11.75
Ni(II)	106.17	1.78	572.46	8.38	0.21
Cd(II)	24.19	4.39	953.17	0.60	7.31

3.4. Reusability of IIP-PANI/HPS adsorbent

To evaluate the recoverability and reusability as a main factor for the practical application of IIP-PANI/HPS, desorption process was performed using 0.1 mol L^{-1} nitric acid as an eluent in optimum conditions. After separation the phases, the adsorbent was washed with deionized water. The recovered material was used for another adsorption experiment. The adsorption-desorption cycles were repeated six times and the amount of the lead ion adsorption after each cycle is shown in Fig. 8. Although a slight decrease was seen in the adsorption capacity of the adsorbent, it could remove more than 90% of lead ions even after six cycles. The results illustrated

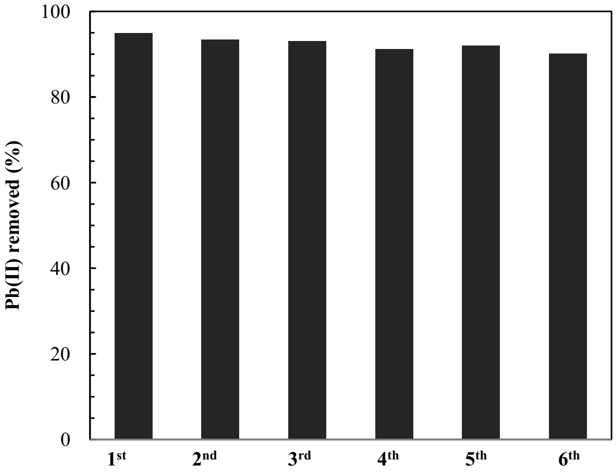


Fig. 8. Variation in lead ions uptake from aqueous phase by IIP-PANI/HPS adsorbent in six adsorption-desorption cycles. The results are average of three independent experiments with a standard deviation (1σ*n*–1) ≤3.9%.

Table 5
Comparison of some of the characteristics presented by the investigated adsorbent in this work for the adsorption of lead ions with those reported in the literature with some other related materials

Imprinted adsorbent	Reusability (times)	Removal (%)	Ref.
IIP in nano-TiO_2 matrix	4	95	[24]
IIP of the vinylpyridine	Not reported	99	[25]
IIP-chitosan on ordered mesoporous silica SBA-15	Not reported	97	[27]
IIP-magnetic chitosan/ graphene oxide	5	90	[34]
IIP -vinyl-functionalized Fe_3O_4	Not reported	99	[30]
IIP-PANI/HPS	6	95	This work

that the Pb(II)-IIP-PANI/HPS shows appropriate reusability and stability in the process.

3.5. Comparison with other reported adsorbents

A comparative study of the results of the present work with the previous reported methods for adsorption of Pb(II) ion is shown in Table 5. The results clearly revealed that the Pb(II) ion-imprinted polymer based on the hyper-cross-linked polystyrene (IIP-PANI/HPS) can be categorized among the good sorbents for simple, selective separation and reusability.

4. Conclusions

Lead(II) ion imprinted polymer was prepared using the combination of Pb(II) as template, aniline as the functional monomer, ammonium per sulfate as the initiator and hyper-cross-linked polystyrene as porous support. The prepared ion-imprinted nanocomposite possess high removal percentage and excellent selectivity for Pb(II) ion over a range of associated metal ions. The adsorption behavior of Pb(II) by IIP can be well described with pseudo-second order kinetic model. The experimental data were fitted appropriately by the Langmuir adsorption isotherms. It was shown that the process is a chemical sorption. It was also demonstrated that the sorbent can be reused for 6 times in adsorption-desorption cycles without significant loose of its adsorption efficiency. The characteristics of the investigated adsorbent towards lead ions allows categorize this material potential and efficient adsorbents for these ions. Such a suitable adsorption efficiency and selectivity could be attributed to the high surface area of the nanoscale polyaniline particles, porosity of matrix polymer, swelling ability of the polymer, uniform distribution of the recognition sites and more favorable accessibility of binding sites in the imprinted cavities.

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