Removal of Pb(II) and Co(II) ions from aqueous solution and industrial wastewater using ILNO-NH₂: Kinetic, isotherm and thermodynamic studies

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Abstract

The efficiency of a novel ionic liquid based nanoporous organosilica supported propylamine (ILNO-NH₂) in the removal of Pb(II) and Co(II) ions from aqueous solution and industrial wastewater has been investigated. The effect of contact time, adsorbent dose, solution pH and concentration of metal ions in batch systems was studied in the adsorption of Pb(II) and Co(II) ions onto ILNO-NH₂. The results indicated that adsorption process was strongly affected by pH and temperature. The experimental data were analyzed using the Langmuir, Freundlich and Temkin isotherm models. Correlation coefficients were determined by analyzing each isotherm. It was found that the Langmuir isotherm showed better correlation with the experimental data than the Freundlich and Temkin ones. According to the parameters of the Langmuir isotherm, the maximum adsorption capacity of ILNO-NH₂ for Pb(II) and Co(II) was found to be 22.27 and 5.20 mg/g, respectively. The kinetics study also showed that the overall adsorption process was successfully fitted with the pseudo-second-order kinetic model.

Moreover, thermodynamic parameters suggested that adsorptions were endothermic and spontaneous.

Keywords: Ionic liquid; nanoporous organosilica; adsorption; isotherm; kinetic

1. Introduction

The growing pollution of heavy metal ions of wastewaters is accompanied with the intensive industrial development of the modern society. Many kinds of toxic heavy metal ions are discharged from several industries such as metal plating facilities, mining operations, nuclear power plant, tanneries and battery manufacturing industries [1]. Cadmium, cobalt, lead and mercury are among the most popular toxic metals associated with these properties. These metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [2]. One of the most widely disturbed ions in the environment is Pb(II) that is very toxic and may cause mental retardation, encephalopathy, seizures and reduce hemoglobin production [3, 4]. Accordingly, rigorous standards for Pb concentrations in industrial effluents have been established by local legislations [5]. Another popular toxic metal is cobalt that exists in the form of various salts in environment. This is widely used in nuclear medicine, as a foam stabilizer in beer, enamels and semiconductors, grinding wheels, painting on glass and porcelain, hygrometers and electroplating, in vitamin B12 manufacture, varnishes and paints, and as a catalyst for organic chemical reactions [6]. It is also important to note that the small amounts of cobalt is essential for human health, because it is known to be an essential element at trace level in human beings, animals and plants for metabolic processes [7]. However, in high concentrations this metal can cause several health troubles such as lung irritations, low blood

pressure, paralysis, bone defects, diarrhea, as well as it may also cause mutations in living cells [8-10]. Therefore, removing and/or elimination of these metals from industrial wastewaters and/or environment are very significant topic between scientists. To date, several methods have been developed to eliminate lead and cobalt ions from wastewater. These include precipitation [11], membrane filtration [12], adsorption [13], ion exchange [14], etc. Among these, adsorption is more promising treatment approach because this is simple, cost-effective and extensively used. Several adsorbents such as natural zeolites [15], chitosan [16], and sodium alginate [17] have been used to remove heavy metal ions from wastewaters. However, these materials suffer from either low adsorption capacity and/or low efficiency. Therefore, it is highly desirable to develop novel adsorbent materials with large surface area and high adsorption capacity for removing toxic heavy metals. Nowadays, nanomaterials have gradually developed as important sorbents to resolve aforementioned problems due to their high surface area, enhanced active sites and abundant functional groups on the surfaces. Especially, ordered mesoporous organosilicas (OMOs) are more attracted in this regard. More recently, we have developed a novel strategy for the preparation of ionic liquid based OMOs and studied their application as efficient support for immobilization of several catalysts in some chemical processes [18, 19]. These have also been applied as effective sorbent in the removal of dyes from wastewaters [20]. In continuous of these important studies, herein, an ionic liquid based nanoporous organosilica supported propylamine (ILNO-NH₂) is prepared, characterized and its adsorption capacity in the removal of lead and cobalt metal ions from aqueous solution is investigated. The ILNO-NH₂ was prepared by hydrolysis and co-condensation of 1,3-bis(trimethoxysilylpropyl)imidazolium chloride and tetramethoxysilane in the presence of pluronic P123 under acidic conditions followed with modification by 3-aminopropyl-trimethoxysilane under reflux conditions (Scheme 1).

2. Experimental

2.1. Instruments and reagents

The following chemicals were commercially available: 3-aminopropyl-trimethoxysilane (97 %, Aldrich), NaOH, HCl, HNO₃, Co(NO₃)₂, Pb(NO₃)₂, EtOH, and toluene (Merck). The metal concentration was determined using an AA-680 Shimadzu (Japan) atomic absorption spectrometer in the flame mode, while the pH/ion meter model-686 thermometer Metrohm was used for measurement of pH adjustment (Metrohm, Switzerland, Swiss). Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed using a Bruker-Vector 22 with KBr disks of powdered samples. Energy dispersive X-ray (EDX) was recorded using a Seron AIS 2300 instrument (Korea). X-ray diffraction (XRD) pattern of the sorbent was obtained by XRD diffractometer (X'pert, Philips). The morphology of the ILNO-NH₂ was taken by the scanning electron microscopy (SEM, KYKY-EM 3200) and transmission electron microscopy (TEM) and image was obtained using instrument model of FEI Tecnai TF20. The stock solutions (1000 mgL⁻¹) of metal ions were prepared by dissolving adequate amount of each salt in 500 mL de-ionized water. All working solutions were prepared in de-ionized water to achieve the desired concentration.

2.2. Preparation of ILNO-NH₂ nanostructure

To do this, firstly the ILNO was prepared according to our recently reported procedure [18, 19]. The IL-NO was then modified by 3-aminopropyl-trimethoxysilane *via* a grafting approach. Typically, ILNO (1 g) was added to a flask containing dry toluene (50 mL) and stirred at room temperature. After homogeneous distribution of ILNO, 3-aminopropyl-trimethoxysilane (0.5 mmol) was added and the obtained mixture was refluxed under argon atmosphere for 24 h

[19]. After cooling reaction mixture to room temperature, the resulted material was filtered and washed thoroughly with dry toluene to remove unreacted aminopropyl-trimethoxysilane. The final precipitate was dried at 70 °C for 12 h and delivered a white powder denoted as ILNO-NH₂ (Scheme 1).

2.3. Batch adsorption experiments

Batch adsorption experiment was performed in 200 mL conical flasks containing 50 mL of single metal nitrate solution, stirring at 160 rpm at temperature of 45 °C. The equilibrium study was carried out by sampling at regular intervals of 3 min. A stock solution of each Pb(II) and Co(II) ions was prepared by dissolving an exact amount of Pb(NO₃)₂ and Co(NO₃)₂ in de-ionized water (conductivity<0.04 μS/m) diluting daily to prepare standard solutions. After sorption, the solution and solid phase were separated by centrifugation at 7000 rpm for 10 min, the supernatant was measured using atomic absorption spectrophotometer. The amount of adsorption was calculated based on the difference of Pb(II) and Co(II) concentration in aqueous before and after adsorption according to the following equation:

$$q_e = (C_0 - C_e)V / W \quad (1)$$

Where q_e is the equilibrium adsorption capacity of ion (mg g⁻¹), C_0 is the initial concentration of metal ion (mg L⁻¹), C_e is the equilibrium concentration of metal ion (mg L⁻¹), V is the volume of the metal ion solution (mL) and W is the adsorbent dosage (mg). The adsorption percentage was defined as follows:

$$Adsorption(\%) = ((C_0 - C_t) / C_0) \times 100 \quad (2)$$

3. Results and discussion

3.1. Characterization of ILNO-NH₂ nanostructure

The DRIFT spectroscopy was used to determine the functional groups of ILNO-NH₂ nanostructure (Figure 1). The stretching vibrations of O-H and N-H bonds of material surface were observed between 3400-3410 cm⁻¹ [21, 22]. The peak observed at 2948 cm⁻¹ is attributed to stretching vibration of aliphatic C-H bonds. The strong bands cleared at 1064 and 946 cm⁻¹ are attributed to asymmetric and symmetric stretching vibrations of Si-O-Si bonds. Moreover, the absorption peaks of other functional groups were observed at 1629 cm⁻¹ (C=N stretching vibration of imidazolium ring) [23], 1565 cm⁻¹ (C=C stretching vibration of imidazolium ring), 1452 cm⁻¹ (C-H deformation vibrations), 1409 cm⁻¹ (bending vibration of aliphatic groups), 796 cm⁻¹ (for C-Si stretching vibrations) and 453 cm⁻¹ (bending vibration of Si-O-Si), respectively. These data successfully confirm successful incorporation and immobilization of alkyl imidazolium ionic liquid and propylamine groups in the material framework.

Chemical composition of ILNO-NH₂ before and after metal ions adsorption was obtained by energy-dispersive X-ray (EDX) spectroscopy. Figure 2a shows the presence of silicon, oxygen, nitrogen, carbon and chloride in the sample before adsorption process confirming the successful immobilization and incorporation of ionic liquid and amine functional groups in the material network. Interestingly, after adsorption process both lead and cobalt were detected in the EDX spectra (Figures 2b, 2c) proving successful adsorption of the metal ions onto/into the ILNO-NH₂ material. The powder X-ray diffraction (PXRD) of ILNO-NH₂ is shown in Figure 3. This analysis illustrated a peak with high intensity at 2θ of 0.90 and two additional peaks with lower intensity at 2θ of 1.49 and 1.70 which indexed as d100, d110 and d200 reflections,

respectively. This is characteristic of materials with highly ordered 2-dimensional hexagonal mesostructure confirming that the material possesses a highly ordered nanostructure [24]. The TEM image of the ILNO-NH₂ was in good agreement with PXRD analysis and showed highly ordered hexagonal arrays of mesopores with uniform pore size (Figure 4). These data strongly confirm high stability of the material during synthesis process and also prove its high adsorption capacity for the removal of metal ions. The scanning electron microscopy (SEM) analysis was carried out to characterize both morphology and particle size of the material (Figure 5). This analysis showed the presence of particles with a regular rope-like morphology in the size distribution range of 50–90 nm for the material. After characterization, the adsorption efficiency of the ILNO-NH₂ was investigated in the removal of Pb(II) and Co(II) from aqueous solution under different conditions of pH, contact time, adsorbent dose, initial metal ions concentration and temperature.

3.2. Effect of pH

The effects of the solution pH can be associated with a number of mechanisms such as metal speciation in solution, change of the ionic forms of the functional groups on the silica surface, and the competition effects of proton ions with metal ions [25]. Figure 6a shows the effect of the pH on the removal of Pb(II) and Co(II) metal ions as the function of the solution pH in the range of 2–8, obtained with the initial metal concentration of 30 mg/L and 0.15 g ILNO-NH₂. As shown, the metal uptake is increased with increasing the pH from 2 to 5 for Pb(II) and 7 for Co(II), while at the pH value higher than 5 and 7 for Pb(II) and Co(II), respectively, the adsorption is decreased. As shown in Figure 6a, at pH 2 the removal efficiency was 42.3% and 18.1% for Pb(II) and Co(II), respectively, and these values increased to 97.5% for Pb(II) at pH 5

and 88.4% for Co(II) at pH 7. This is because at low pH values there is an excessive protonation of the amine groups, resulting in a decrease in the sorption of heavy metal ions [25]. Therefore, the increase in the metal removal with increasing pH can be explained on the basis of a decrease in competition between proton ions (H^+) and positively charged metal ions at the adsorbent surface sites. It is also important to note that at the pH more than 8, the adsorption could not be carried out due to precipitation of $Pb(OH)_2$ and $Co(OH)_2$. Therefore, the experiments were performed with the pH value of 5 for Pb(II) and 7 for Co(II). To explain this observation, the presence of dominant metal ions M(II) species at $pH > 8$ is $M(OH)_2$ and at $pH < 8$ is M^{2+} and $M(OH)^+$, therefore, most ions are not accessible to adsorb at higher pH values and consequently the removal efficiency is decreased.

3.3. Effect of adsorbent dosage

In order to compare the removal efficiency of Pb(II) and Co(II) ions, the effect of the dose of ILNO-NH₂ was studied. Figure 6b shows that 0.15 g/50 mL of ILNO-NH₂ can remove 97.5% Pb(II) and 88.4% Co(II) from aqueous solution [26]. In fact, the amino groups on ILNO-NH₂ interact with heavy metal ions by complexation mechanism which is necessary for removing them from aqueous solution.

3.4. Effect of initial ion concentration

As shown in Figure 6c it was clear that with increasing metal ion concentration the removal of Pb(II) and Co(II) metal ions decreased gradually. High initial ion concentration provided less driving force to overcome various mass transfer resistances of the metal ions from

the aqueous to the solid phase resulting in higher collision between metal ions and ILNO-NH₂ surface increasing the uptake of ions [27]. In addition, the extent of adsorption comes down for a fixed adsorbent content at high metal ion concentration due to decrease in the number of available adsorption sites of the adsorbent surface [28].

3.5. Effect of contact time

The influence of contact time on the adsorption of metal ions by the ILNO-NH₂ is illustrated in Figure 7. According to this Figure, it can be seen that the adsorption of metal ions on ILNO-NH₂ increased as the contact time increased. In the first minutes of adsorption, due to the high concentration of metal ions in solution, the number of effective interactions between the metal ions and the adsorption sites on the surface ILNO-NH₂ are increased. Moreover, with the progress of time, the concentration of the metal ions is decreased and the adsorption sites are mostly saturated. The adsorption of Pb(II) and Co(II) onto ILNO-NH₂ reached to equilibrium within 39 and 45 min, respectively. Hence, in the next studies, 39 and 45 min were chosen as the equilibrium time for Pb(II) and Co(II), respectively.

3.6. Adsorption equilibrium study

To understand the adsorption mechanism of metal ions on the ILNO-NH₂, the adsorption data were analyzed by adsorption isothermal models. Here, Langmuir, Freundlich and Temkin adsorption isotherm models were used to describe the equilibrium between adsorbed metal ions on ILNO-NH₂ (q_e) and metal ions in solution (C_e) at a constant temperature [29]. The Langmuir model assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application in

many monolayer adsorption processes. The linear form of the Langmuir isotherm is depicted by the following equation:

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

Where q_e represents the amount of metal ion adsorbed on the adsorbent at equilibrium (mg g^{-1}); C_e describes the equilibrium metal ion concentration (mg L^{-1}); Q_m denotes the maximum adsorption capacity corresponding to complete monolayer coverage and K_L is the Langmuir adsorption equilibrium constant (L mg^{-1}). Thus, a plot of C_e/q_e vs C_e (Figure 8a) results in a straight line of slope ($1/Q_m$) and an intercept of $1/K_L Q_m$. From the slopes and intercepts, the values of Q_m and K_L were calculated and are given in Table 1.

The Freundlich model is applied to monolayer adsorption as Langmuir model but this is not a saturation-type isotherm. Freundlich model is used to estimate the sorption intensity of the adsorbent toward the adsorbate and it can be represented as follows:

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e) \quad (4)$$

Where K_F is Freundlich constant indicating adsorption capacity, n is an empirical parameter related to the intensity of adsorption. They can be calculated from the intercept and slope of linear plot of $\ln q_e$ vs $\ln C_e$, respectively. The values of K_F and n are shown in Table 1. The heat of the adsorption and the adsorbent–adsorbate interaction were also evaluated by using Temkin isotherm model. The derivation of the Temkin isotherm assumes that due to adsorbate/adsorbent interaction, the heat of adsorption decreases linearly rather than logarithmically, as implied in the Freundlich equation [30]. The well-known linear form of Temkin isotherm is as following:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (5)$$

Where $B_T = RT/b_T$, T is the absolute temperature in K, R the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, K_T the equilibrium binding constant (L mg^{-1}) and B_T is related to the heat of adsorption. A plot of q_e versus $\ln C_e$ enables the designation of the equation constants K_T and B_T . The Langmuir, Freundlich and Temkin parameters for the adsorption of Pb(II) and Co(II) onto ILNO-NH₂ are summarized in Table 1. Based on the R^2 values, it is clear that the Langmuir model is fitted with the experimental data better than the Freundlich and Temkin models (Table 1).

3.7. Kinetics evaluation

Kinetics of the adsorption process is very important in wastewater treatment, as it provides essential information on the reaction pathways and the solute uptake rate. The conventional kinetic models include pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion were used to explain the adsorption mechanism. The linear forms of pseudo-first-order [31] and pseudo-second-order equations [32] are expressed as:

$$\log(q_e - q_t) = \frac{\log q_e - k_1 t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where q_e and q_t are the adsorption capacity (mg/g) at equilibrium and time t (min), respectively, k_1 (min^{-1}) and k_2 ($\text{g}/(\text{mg min})$) are the rate constants. By plotting the values of $\log(q_e - q_t)$ versus t , and t/q_t versus t for pseudo-first-order and pseudo-second-order equations, respectively, a linear relationship may obtain that k_1 , k_2 and q_e values can be determined from the slope and intercept of the obtained lines. The low value rate constant of pseudo-second-order equations (k_2) suggests that the adsorption rate decreased with increasing time and

the adsorption rate was proportional to the number of unoccupied sites [33]. The Elovich equation as another rate equation, based on the adsorption capacity in linear form, has been successfully applied for the adsorption of solutes from a liquid solution according to the following equation [34]:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad (8)$$

Where α is the initial adsorption rate ($\text{mg g}^{-1} \text{ min}$) and β is the desorption constant (g/mg). The plot of q_t versus $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$ if the Elovich model is applicable. Adsorption kinetic is usually controlled by different mechanisms. One of the most general ones is the diffusion mechanism which can be explained by intraparticle diffusion model proposed by Weber and Morris [35]. This model can be expressed as:

$$q_t = K_{id} t^{1/2} + C \quad (9)$$

Where k_{id} is the intraparticle diffusion constant ($\text{mg/g.min}^{0.5}$) and the intercept (C) reflects the boundary layer effect. The values of K_{id} and C were calculated from the slope and intercept of the plot of q_t versus $t^{1/2}$. The estimated kinetic models and related parameters with linear regression coefficient (R^2) for the adsorption of lead and cobalt using ILNO-NH₂ are presented in Table 2. The values of R^2 showed that pseudo-second-order model is better fitted to the experimental data than other Kinetic models (Figure 8b). In addition, the calculated equilibrium adsorption capacities (q_{cal}) from the pseudo-second-order adsorption kinetics were very close to the experimental data (q_{exp}). The adsorption kinetics followed the pseudo-second-order equation indicating chemical sorption as the rate-limiting step of adsorption mechanism [36].

3.8. Effect of temperature and thermodynamic studies

The effect of temperature on the sorption of Pb(II) and Co(II) ions by ILNO-NH₂ were investigated at a constant concentration (30 mg L⁻¹), temperature (25–50 °C), pH 5 for Pb(II) and 7 for Co(II), stirring rate 160 rpm and adsorbent dosage 0.15 g/50 mL of ILNO-NH₂. The thermodynamic parameters were calculated from the slope and intercept of lnK_c against 1/T by using the following equation [37]:

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (10)$$

where K_C is the standard thermodynamic equilibrium constant, ΔH^0 , ΔS^0 , R, and T are the enthalpy change, entropy change, gas constant, and absolute temperature (K), respectively. Gibbs change (ΔG^0) of sorption was calculated from the following equation:

$$\Delta G^0 = -RT \ln K_c \quad (11)$$

The values of thermodynamic parameters for the sorption of Pb(II) and Co(II) ions on ILNO-NH₂ are presented in Table 3. The enthalpy change of sorption suggests the possibility of strong bonding between sorbate and sorbent. The positive value of ΔH^0 indicates the endothermic nature of the sorption process. The removal of water molecules from the solid/solution interface and from the sorbing cations may be the reason for endothermicity of the heat of sorption [38]. The Gibbs free energy change (ΔG^0) is negative, indicating that the sorption process is more favorable at higher temperatures and spontaneous in nature. The positive value of ΔS^0 also suggests some structural changes in the sorbate and the sorbent indicating the increased randomness at the solid/solution interface during the sorption process.

3.9. Comparison of various adsorbents

The removal of Pb(II) and Co(II) ions by different adsorbents has been studied extensively, and adsorption capacity were reported in literatures. Table 4 compares the adsorption capacity of the present adsorbent with different previously adsorbents used in the removal of Pb(II) and Co(II) ions [39-45]. It can be seen from this comparison that the adsorption capacities of the ILNO-NH₂ adsorbent are much higher than previously reported adsorbents, indicating that the prepared adsorbent has great potential application in the Pb(II) and Co(II) ions removal from aqueous solution. The higher adsorption capacity of the ILNO-NH₂ could be attributed to uniform porous structure of the material and also presence of amino functional groups onto the surface of the ILNO-NH₂ increasing the effective interaction between solid and metal ions.

4. Conclusion

In summary, for the first time, the removal efficiency of a novel ionic liquid based nanoporous organosilica supported propylamine (ILNO-NH₂) was studied in the removal of Pb(II) and Co(II) metal ions from aqueous solution *via* adsorption method. The results showed that the adsorption capacity of the material is affected by the solution pH, concentration of the metal ions, dosage of adsorbents and contact time. The optimized pH was 5 and 7 for adsorption of Pb(II) and Co(II) ions, respectively. It was also found that the Langmuir model is the best model to describe adsorption behavior of these ions onto ILNO-NH₂. According to Langmuir equation the maximum adsorption values of Pb(II) and Co(II) was 22.27 and 5.20 mg/g, respectively. In addition, the kinetic study demonstrated that the adsorption process followed the pseudo-second-order model. Thermodynamic studies also suggested that the adsorption process of aforementioned metal ions onto the ILNO-NH₂ is endothermic and entropy favored in nature. Finally, we found out that our new synthesized ILNO-NH₂, due to possess of uniform porous

channels and suitable organic functional groups, is a powerful and efficient adsorbent for the removal of heavy metal ions from water and wastewater.

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Scheme caption:

Scheme 1. Preparation of ILNO-NH₂ nanomaterial

Scheme 1.

Figures caption:

Fig. 1. DRIFT spectrum of NOIL-NH₂

Fig. 2. Energy dispersive X-ray (EDX) spectroscopy of the (a) NOIL-NH₂ (b) after the adsorption of lead and (c) after the adsorption of cobalt

Fig. 3. X-ray diffraction (XRD) pattern of NOIL-NH₂ nanostructure

Fig. 4. Transmission electron microscopy (TEM) image of the NOIL-NH₂

Fig. 5. Scanning electron microscopy (SEM) image of the NOIL-NH₂

Fig. 6. Effect of (a) pH; (b) adsorbent dosage and (c) initial ion concentration on the removal of lead and cobalt using NOIL-NH₂

Fig. 7. Effect of contact time on the removal of lead and cobalt using NOIL-NH₂

Fig. 8. (a) The Langmuir isotherm and (b) pseudo-second order kinetic plots for the adsorption of lead and cobalt on NOIL-NH₂

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Table 1

Isotherm constant parameters and correlation coefficients calculated for the adsorption of lead and cobalt onto NOIL-NH₂

Isotherm	Parameters	Ion	
		Pb	Co
Langmuir	Q _m (mg/g)	22.27	5.20
	K _a (L/mg)	0.57	2.74
	R ²	0.996	0.995
Freundlich	1/n	0.08	0.14
	K _F (L/mg)	9.86	7.62
	R ²	0.974	0.959
Tempkin	B ₁	0.95	1.60
	K _T (L/mg)	28853	80.31
	R ²	0.911	0.965

Table 2

Kinetic parameters for the adsorption of lead and cobalt onto NOIL-NH₂

Model	Parameters	Ion	
		Pb	Co
First-order kinetic	k ₁	0.19	0.14
	q _e (calc)	53.39	39.61
	R ²	0.839	0.888
Second-order kinetic	k ₂	0.004	0.002
	q _e (calc)	13.66	13.42
	R ²	0.990	0.974
Intraparticle diffusion	K _{id}	1.52	1.42
	C	0.27	-0.91
	R ²	0.940	0.925
Elovich	β	0.32	0.31
	α	1.76	1.05
	R ²	0.984	0.967

Table 3Thermodynamic parameters for the adsorption of lead and cobalt onto NOIL-NH₂

Ion	T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
Pb	298.15	-2.57	99.46	340.42
	303.15	-3.15		
	308.15	-4.68		
	313.15	-7.49		
	318.15	-9.76		
	323.15	-9.96		
Co	298.15	-2.82	33.09	120.15
	303.15	-3.22		
	308.15	-3.74		
	313.15	-4.58		
	318.15	-5.36		
	323.15	-5.55		

Table 4Comparison of the maximum monolayer adsorption (q_m) of lead and cobalt onto various adsorbents

Ion	Adsorbent	q_m (mg/g)	Reference
Pb	Activated carbon-zeolite composite	2.65	[39]
	Heartwood of Areca catechu powder	11.72	[40]
	Biosorbent (Cephalosporium aphidicola)	0.924	[41]
	Agricultural waste	20	[42]
	NOIL-NH ₂	22.27	Present work
Co	Kaolinite	0.919	[43]
	Pine sawdust	0.011	[44]
	Anaerobic granular sludge	12.46	[45]
	NOIL-NH ₂	5.20	Present work

Graphical Abstract