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Removal of Pb(II) ions using modified-NiO nanoparticles

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ABSTRACT

Removal of Pb(II) ions from aqueous solutions using modified-NiO nanoparticles (m-NONPs) prepared through chemical reaction of NiO nanoparticles (NONPs) with 3-aminopropyltriethoxysilane was investigated in a batch system. The influence of experimental conditions including contact time, pH, Pb(II) concentration and presence of diverse ions on Pb(II) adsorption was studied. The results indicated that the adsorption process correlated with the Langmuir and Freundlich models. The maximum adsorption capacity of m-NONPs was found to be 100.2 mg g⁻¹ which is considerably more than that of NONPs. The results suggest that m-NONPs is potentially efficient for removing Pb(II) ions from aqueous solutions. © 2014 Trade Science Inc. - INDIA

KEYWORDS

NiO;
 Lead;
 Modification;
 Adsorption;
 Nanoparticle.

INTRODUCTION

The growth of the industrial activities has increased the pollution in the environment, mainly, in aquatic ecosystems^[1,2]. Waste stream from many industries such as tannery, chemical manufacturing, mining, metallurgical processes, metal plating, oil refinery, pigments and alloy industries contains considerable amount of toxic and polluting heavy metals which represents a serious problem to human health and ecological systems^[3,4]. Among the toxic heavy metals, special attention has been given to lead due to its high toxicity, causing many health problems to the human such as anaemia, paralysis, coma, kidney dysfunctions, brain damage, bone diseases, skin and lung cancer, etc^[5]. Removal of this toxic metal from environment is thus a major focus of waste treatment.

Many physicochemical methods have been used for heavy metals removal from aqueous solutions including

chemical precipitation, ion exchange, electrochemical reduction, membrane separation and adsorption^[6-12]. Among these methods, adsorption is preferred to remove heavy metal ions because of its high efficiency, availability of different adsorbents, easy handling and cost effectiveness^[13]. Several metal oxides have been used for metal ions sorption. Whereas numerous studies have been reported about the adsorption of heavy metals on iron oxide, titanium oxide, zinc oxide and silica, very little is reported about the metal ions adsorption onto other metal oxides such as cobalt oxide and nickel oxide^[14-20].

Compared to the traditional materials, nanomaterials possess more efficient performance because of their high specific surface area. Furthermore, by the surface modification, their capability for metal adsorption can be improved. The ligands containing nitrogen atom have excellent adsorption capability for metal cations due to the strong affinity between nitrogen atom and metal cat-

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ions^[21-23]. In the previous work, removing of Pb(II) ions from aqueous solutions using NiO nanoparticles was described^[20]. In this study, the NiO nanoparticles (NONPs) were modified by aminopropyltriethoxysilane (APTES) and the modified-NiO nanoparticles (m-NONPs) used as new adsorbent for removing of Pb(II) ions. Therefore, the objective of this study is comparison of the adsorption capability of NONPs with m-NONPs for Pb(II) removal from aqueous solutions.

EXPERIMENTAL

Chemicals

Analytical grade of nitric acid (HNO₃), sodium hydroxide (NaOH), 3-aminopropyltriethoxysilane (APTES), ethanol, Pb(II) nitrate, copper (II) nitrate, cadmium (II) nitrate, cobalt (II) nitrate, zinc(II) nitrate, Al(III) nitrate and chromium chloride (CrCl₃), were purchased from Merck Co. Nickel oxide (NiO) was obtained from Loba Chemie Co. (India). Standard stock solutions of 1.0 g L⁻¹ ions were prepared by dissolving appropriate amounts of the corresponding salts in double distilled water and were diluted prior to use.

Equipments

The FT-IR spectra were recorded from 400 cm⁻¹ to 4000 cm⁻¹ with Bruker Tensor 27 (Germany) spectrometer using the KBr pellet technique. The concentration of metal ions was measured by a Varian Spectra AA 100 atomic absorption spectrometer using an air-acetylene flame.

A KQ 100 Controllable Ultrasonic apparatus (Kunshan apparatus company, China) was applied to disperse nano-NiO in solution, operating at an ultrasonic frequency of 20-80 KHz and an output power between 0 and 50 W through manual adjustment. The solution pH was adjusted with a Metrohm 827 Model pH-meter (Switzerland) supplied with a glass combined electrode. A Heidolph model MR 3001K magnetic stirrer was used for mixing the adsorbent and aqueous solutions.

Preparation of modified-NiO nanoparticles with APTES

Firstly, the NiO nanoparticles (NONPs) with a mean diameter 20 nm were prepared according to our previ-

ous work^[24]. Secondly, for surface modifying of the prepared NONPs by APTES, 1.0 g of NONPs was added to 25 mL of ethanol under sonication for 1h, then 4 mL of APTES was added and the reaction mixture was magnetically stirred (600 rpm) for 4h. The mixture decanted and washed with ethanol and acetone for three times to remove excess APTES. Finally, the powder was dried at 60 °C under vacuum. The modified-NiO nanoparticles (m-NONPs) were then characterized by FT-IR before employing.

Adsorption experiments

Batch adsorption experiments were performed in 100 mL conical flasks by mixing a known amount of the m-NONPs with 50 mL Pb(NO₃)₂ aqueous solution of varying concentration at 25±1 °C under stirring at 180 rpm. After appropriate time, the suspension was centrifuged at 6000 rpm for 10 min and the concentration of Pb(II) in the supernatant was determined by a flame atomic absorption spectrometer (FAAS). The adsorption capacity (q) of the m-NONPs for Pb(II) sorption was calculated from the following formula:

$$q = (C_0 - C_t) \times V/m \quad (1)$$

where q is the amount of Pb(II) adsorbed per unit mass of m-NONPs (mg g⁻¹); C₀ is the initial concentration (mg L⁻¹) of Pb(II); C_t is the concentration of Pb(II) after a certain period of time (mg L⁻¹); V is the initial solution volume (L) and m is the m-NONPs mass adsorbent (g). The effect of contact time, solution pH, initial concentration of Pb(II) solution (C₀) and diverse ions on the Pb(II) adsorption was investigated at 25 °C.

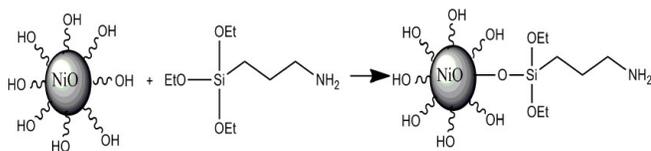
Adsorption isotherm studies were conducted by mixing 0.01 g of m-NONPs with 50 mL of Pb(NO₃)₂ aqueous solutions of different concentrations, varying from 20 to 100 mg L⁻¹ at 25 ± 1 °C and pH of 7 for 4h. The pH of test solution was adjusted to the desired value using 0.1M HNO₃ or 0.1 M NaOH. A control Pb(II) solution in the absence of m-NONPs was run in parallel with each experiment under same experimental conditions. All experiments were performed in triplicate and the average values are reported here.

RESULTS AND DISCUSSION

Preparation of m-NONPs

As it is known, metal oxides nanoparticles have po-

tential to be surface-modified with functional compounds due to presence of hydroxyl groups on their surface^[25-28]. Accordingly, m-NONPs was prepared through reaction of NONPs with APTES. The diagram of modification of NiO nanoparticle by APTES is represented in the scheme 1.



Scheme 1 : Preparation of m-NONPs.

The FT-IR technique as a reliable method for following the variations in the functional groups was used for characterization the prepared m-NONPs. Figure 1 shows the FT-IR spectra of NiO (a) before and (b) after reaction with APTES. From comparison of spectra (a) and (b), it is observed that a new peak appeared at 1050 (Figure 1b) which is attributed to Si-O stretching bond. This reveals that hydroxyl groups of the surface NiO have been successfully reacted with APTES. A similar procedure was reported for modification of ZnO nanoparticles by APTES^[29].

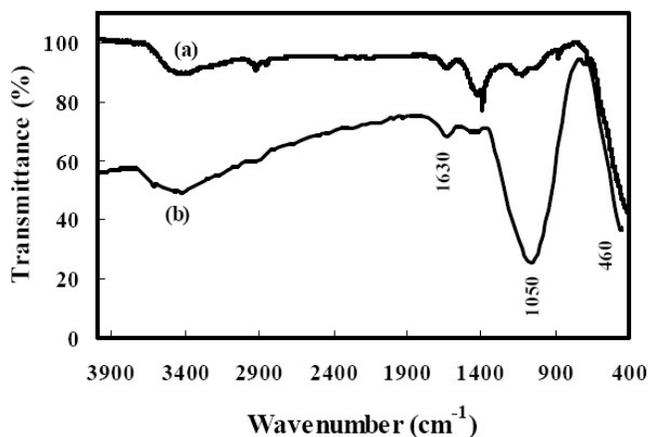


Figure 1 : FT-IR spectra of (a) NONPs (b) m-NONPs.

Pb(II) adsorption

To obtain the optimal conditions for Pb(II) sorption by m-NONPs, the influences of various parameter such as contact time, pH and initial concentration of Pb(II) solution were investigated. The effect of contact time on the Pb(II) sorption by m-NONPs was investigated by mixing 50 mL of 20 mg L⁻¹ Pb(II) solution with 0.01 g m-NONPs. As shown in Figure 2, the rate of Pb(II) uptake is initially fast and then gradually de-

clines, reaching to equilibrium value (C_e) after 4h. Generally, the fast adsorption rates observed within the initial time-course may be related to the existence of the greater number of available sorption sites for adsorption of the Pb(II) ions. Since the number of sorption sites for an adsorbent is fixed, and each active site can adsorb only one ion, decrease of remaining active sites leads to slowdown in adsorption rate due to competition of the remained Pb(II) ions in solution and formation of repulsive forces between Pb(II) ions on solid surface.

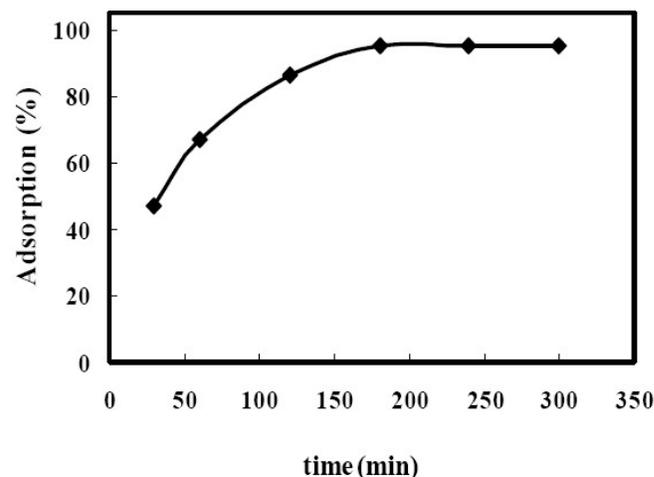


Figure 2 : Effect of contact time on the adsorption efficiency of Pb(II) on the m-NONPs.

The effect of solution pH on the adsorption of Pb(II) ions by m-NONPs was studied by suspension 0.01 g of m-NONPs in 20 mL of 20 mg L⁻¹ Pb(II) solution by varying pH ranging from 3 to 8. To avoid precipitation of Pb(II) ions in hydroxide form (pH >8) and also pre-

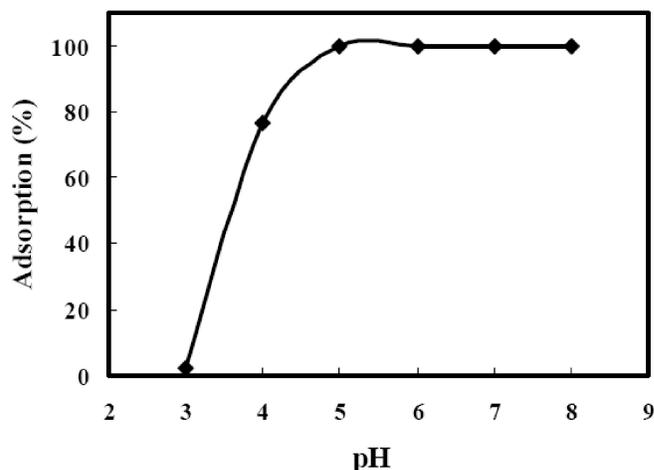


Figure 3 : Effect of pH on the adsorption efficiency of Pb(II) on the m-NONPs.

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vent dissolution of the NiO adsorbent in acidic solution (pH < 2), the adsorption experiments were conducted at $3 < \text{pH} < 8$. The results were shown in Figure 3.

As shown in Figure 3, the adsorption efficiency was highly pH dependent. The Pb(II) adsorption was increased by increasing of the solution pH and then reached a maximum (over 99 %) at pH values > 5. The effect of pH on the adsorption efficiency might be due to the surface properties of the m-NONPs adsorbent, carrying $-\text{NH}_2$ groups and the degree of their protonation which varies by variation of pH value. The influence of pH on the adsorption Pb(II) by m-NONPs can be explained by the following Eqs.:



Eq. 2, indicates the protonation of the amino-groups of m-NONPs, resulting in formation of positively charged surface. Accordingly, as the solution pH decreases, more $-\text{NH}_2$ groups of m-NONPs surface become protonated and converts to $-\text{NH}_3^+$, leading to decrease the available $-\text{NH}_2$ groups on the m-NONPs surface and hence adsorption of Pb(II) ions through Eq. 3 decreases. Additionally, the electrostatic repulsion between Pb(II) ions and the protonated amino-groups of m-NONPs is increased when the pH decreases, causing a decrease in the Pb(II) adsorption.

Effect of diverse ions

In order to investigate the effect of potential interfering ions on the uptake of lead ions by m-NONPs, the adsorption of Pb(II) ions from their binary mixtures

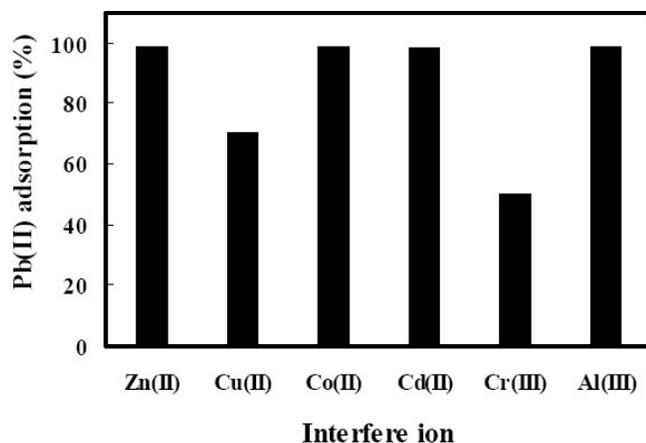


Figure 4 : Adsorption efficiency of Pb(II) by the m-NONPs in the presence of diverse ions.

with diverse ions including Cd(II), Zn(II), Cu(II), Co(II), Cr(III) and Al(III) was examined. The experiments were conducted by mixing 0.01 g m-NONPs with 20 mL of 20 mg L^{-1} Pb(II) solution containing 20 mg L^{-1} of each individual interfere ions and the efficiency of Pb(II) adsorption in the presence of each diverse ions was determined. As it is shown in Figure 4, except Cu(II) and Cr(III), the other diverse ions have no significant influence on the Pb(II) adsorption from the binary mixtures, suggesting the high affinity of m-NONPs toward Pb (II) ions as compared to the other ions.

Adsorption isotherms

The adsorption isotherms of Pb (II) ions at 25°C were obtained by varying the initial concentration of Pb(II) solution from 20 to 100 mg L^{-1} . The experimental results were analyzed by the Langmuir and Freundlich isotherms^[30]. The Langmuir model is valid for monolayer adsorption onto surface containing finite number of identical sorption sites. The linear form of Langmuir model is expressed by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4)$$

where q_e and q_m are the observed and maximum adsorption capacities (mg g^{-1}), respectively, C_e is the equilibrium concentration (mg L^{-1}) and b is Langmuir adsorption constant related to the affinity of binding sites (L mg^{-1}). On the other hand, the Freundlich equation is based on adsorption on heterogeneous surface. The linear form of this model is as bellow:

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (5)$$

where K_f is the Freundlich adsorption capacity and $1/n$ refers to the Freundlich adsorption intensity.

The adsorption parameters of the Langmuir and Freundlich isotherms derived from their related plots (Figures. 5, 6). The good correlation coefficients (R^2) obtained from Langmuir ($R^2 = 0.991$) and Freundlich ($R^2 = 0.980$) models indicate that the adsorption of pb(II) on m-NONPs obeys both models. These results suggest that the adsorption of Pb(II) ions on m-NONPs is monolayer and the adsorption sites are energetically heterogeneous. The values of $1/n$ and $\log K_f$ were found to be 0.155 and 1.68, respectively. The value of $1/n < 1$ indicates that the adsorption of Pb(II)

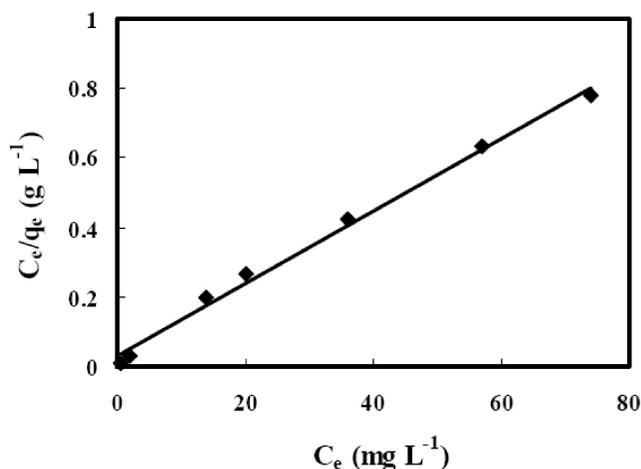


Figure 5 : Langmuir isotherm adsorption plot of Pb(II) on m-NONPs.

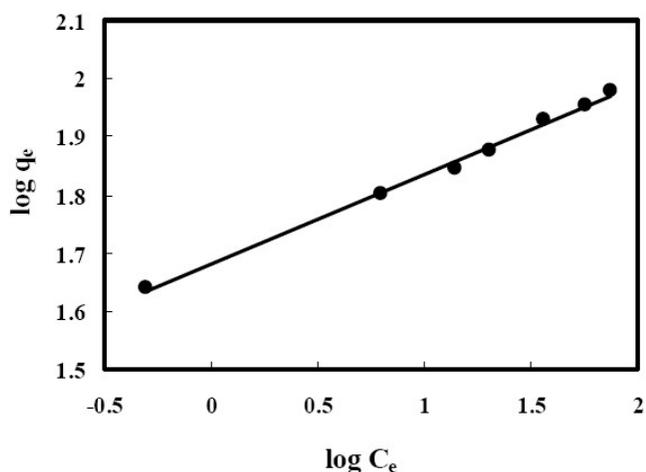


Figure 6 : Freundlich isotherm adsorption plot of Pb(II) on m-NONPs.

ions on the m-NONPs is favourable^[31].

Comparison of the maximum adsorption capacity (q_m) of m-NONPs, obtained from the present study with that of NONPs^[20], indicates that adsorption capacity of m-NONPs (100.2 mg.g⁻¹) is about 1.5 times more than that of NONPs (62.5 mg g⁻¹). This can be attributed to the presence of aminopropyl chain (Scheme 1), carrying N-donor atom, which leads to coordination interactions between Pb(II) and -NH₂ groups and formation of surface complex of NH₂-Pb²⁺.

CONCLUSIONS

The modified-NiO nanoparticles (m-NONPs) were successfully prepared through reaction of 3-aminopropyltriethoxysilane (APTES) with NiO

nanoparticles and employed as new adsorbent for uptake of Pb(II) ions from aqueous solutions. It was found that contact time, pH and initial concentration of Pb(II) solution influence on adsorption capacity, and the adsorption process obeys both Langmuir and Freundlich isotherms. Maximum adsorption capacity of m-NONPs was found to be 100.2 mg g⁻¹ which is remarkably more than that of NONPs (62.5 mg g⁻¹) indicating an improvement in the adsorption properties of NiO nanoparticles surface due to modification by APTES. This result suggests the m-NONPs as a potentially efficient adsorbent for Pb(II) removal from aqueous solutions.

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