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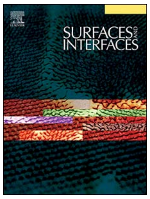

An efficient removal of lead from aqueous solutions using $FeNi_3@SiO_2$ magnetic nanocomposite

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ABSTRACT

The aim of the present study was the synthesis of nickel ferrite magnetic nanoparticles functionalized with SiO_2 using Stöber method for its application to remove lead from the water. To determine the characteristics of the synthesized magnetic nano-composite, different analysis tools were used including, Fourier transforms infrared spectrometer, X-ray diffraction analysis, Vibrating sample magnetometer and Transmission electron microscopy. Results of Vibrating sample magnetometer analysis showed that $FeNi_3@SiO_2$ have typical soft magnetic traits and extraordinary para-magnetism at room temperature. The successful conjugation of SiO_2 onto the surface of $FeNi_3$ nanoparticles was confirmed by Fourier transform infrared spectroscopy. Transmission electron microscopy images of $FeNi_3@SiO_2$ magnetic nano-composite showed particle size of around 30 nm. The optimum conditions for lead removal from the water were obtained at pH 6, 300 mg/L adsorbent dose and 20 min contact time, wherein in these circumstances the removal of lead was 87.31%. The adsorption isotherms primacy was as follows, Freundlich $R^2 = 0.9889 >$ Langmuir $R^2 = 0.9539 >$ Temkin $R^2 = 0.9268$. Also, investigation of adsorption kinetics of pseudo-first and second orders indicated that lead adsorption by $FeNi_3@SiO_2$ followed the pseudo-second-order with the higher correlation coefficient of $R^2 = 0.9994$.

1. Introduction

The rapidly growing of industries have widely increased the concentration of toxic heavy metals like Pb, As, Cd, and Hg in nature and due to the toxic and carcinogenic effects of heavy metals, the exposure to these heavy metals is considered a major health risk [1]. Water pollution by toxic heavy metals is one of the main issues of the environment because heavy metals tend to accumulate, thereby even in very low concentrations are harmful to public health [2–4]. Heavy metal ions can enter the water from both natural and human sources causing serious environmental hazards so must be removed from the water [5]. Compared with other metals, lead is known as one of deadly poisons, which can accumulate in the body through contaminated food and water and when exposed to the human can damage the nervous system, kidneys, liver and reproductive system [6]. Activities such as mining, smelting, printing, metal plating, manufacture of explosives, dyes, and products such as paints, plastics, batteries, ceramics and glass have increased lead emissions to the environment [7]. There are several processes for toxic heavy metals removal, especially methods such as coalescence, chemical sedimentation, membrane, ion exchange, ultrafiltration and sorption. However, most of these methods have limitations such as high operating costs and lack of cost-effectiveness on the large scale. Adsorption has emerged out to be better alternative treatment methods. This method is effective and economical due to its relatively low cost. Furthermore, adsorption id the easiest, safest and most cost-effective methods for the removal of heavy metals from waste effluents containing [8,9]. Compared with other methods, adsorption is also considered as the most effective method to remove lead ions due to advantages such as decline in production of biological or chemical sludge and the probability of restructuring an adsorbent [10]. To remove lead from water, different adsorbents can be used whereby these adsorbents have important sources viz. artificial and natural sources. Benefit of sophisticated adsorbents is the capability to design their structure, for an example, their functionalization and even chemical modification can be carried out [11]. In recent years, magnetic nanoparticles due to their easy separation by means of an external magnetic field have become one of the most useful and efficient absorber's. The nanosorbents with high surface area and small size particles, increasing the chemical reactivity and interactions between adsorbent/adsorbate are highly preferred [12]. Till date, numerous studies have been conducted on lead removal from water by a variety adsorbent. For example, the synthesis of Fe_3O_4 nanoparticle and removal of chromium

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Cr^{6+} and lead Pb^{2+} from water [13] or lead removal by renewable biopolymer composite of chitosan *Agaricus bisporus* and feather *Dromaius novaehollandiae* [14]. Alloy of $FeNi_3$ is one of magnetic materials that is widely used owing to its high permeability and saturation magnetization, besides low energy losses and high temperature [14]. $FeNi_3$ nanoparticles functionalized with SiO_2 can ameliorate the electrical resistor of materials effectively, and minimize losses [15].

In this study, nickel ferrite magnetic nanoparticles were synthesized and functionalized with silica-shell and the nanocomposite was used to remove lead from the water. This study has been carried out in the Laboratory of Environmental Pollutions, the University of Birjand in 2016.

2. Material and methods

2.1. Chemicals

All chemical materials including $FeCl_2.4H_2O$, $NiCl_2.6H_2O$, polyethylene glycol (PEG 6000), Sodium hydroxide and Hydrazine hydrate, purchased from Merck Company and used without further purification.

2.2. Synthesis of nickel ferrite magnetic nanoparticle $FeNi_3$

Initially, $FeCl_2.4H_2O$ (1.988 g) and $NiCl_2.6H_2O$ (7.131 g) were dissolved in 200 mL of deionized water followed by addition of polyethylene glycol PEG 6000 (1 g). Sodium hydroxide solution (5 M) was added to the solution until the pH value reached the range of $12 \leq pH \leq 13$. Hydrazine hydrate (7.1 mL, 80%) was added to the previous solution and the mixture was stirred about 24 hours at room temperature. During this period, the pH value was controlled between $12 \leq pH \leq 13$ by addition of NaOH. Finally, the black powder of $FeNi_3$ magnetic nanoparticles was separated by an external magnet from the solution and rinsed with the deionized distilled water and ethanol, to completely neutralize free of OH ion, and then dried in a vacuum oven at 70 °C for 8 h. In the next step, to prevent oxidation the dried nanoparticles were poured into a container with lid and argon gas was used.

2.3. Synthesis of $FeNi_3/SiO_2$ magnetic nanocomposite

This nanocomposite was made using Stöber method with slight variations. Initially, $FeNi_3$ (2 g) was dispersed in ethanol and water solvent in the proportion of 80% ethanol and 20% water for 30 min at room temperature *via* sonication, then 2 mL of 28wt% concentrated ammonia aqueous solution $NH_3{\cdot}H_2O$ was added to the solution. 4 mL of TEOS, were appended to the solution dropwise, and the mixture was stirred for 20 h at room temperature. Next, the obtained $FeNi_3@SiO_2$ magnetic nanocomposite was separated by an external magnet, washed with deionized water and ethanol to completely neutralize and dried in a vacuum oven at 70 °C for 8 h [16].

2.4. A pilot study of optimization of lead ions

All adsorption experiments were conducted in the laboratory of School of Natural Resources, University of Birjand, at a constant temperature 25 ± 2 °C and in a batch system. In the first stage in order to optimize pH, the concentration of lead 5 mg/L and adsorbent concentration 150 mg/L was considered.

To obtain the desired concentration of pollution, standard solution of lead nitrate $Pb(NO_3)_2$ was used. According to the calculations, to achieve 5 mg/L of lead, 1.25 mL from the standard solution of lead nitrate 1000 ppm was poured in 250 mL flask and made up to the desired volume. Later, the prepared solution was poured in six flasks, 20 mL in each, and pH 3, 4, 5, 6, 7 and 8 were set by introduction of NaOH and HNO_3 solutions in the desired range, then 3 mg adsorbent concentration of 150 mg/L was appended to each of the flasks and placed on the shaker for 20 min. Finally, the solution was filtered and the residual lead was read by atomic absorption machine ConterAA-700.

To determine the equilibrium time, the prepared lead solutions with 5 mg/L concentration, in optimum pH condition and with the addition of 3 mg of adsorbent were placed on a shaker with 200 cycles per minutes for 5, 10, 20, 30, 40 and 60 min, respectively. The solid and liquid phases of solution were separated by filtration and the residual lead was measured. After determining the optimum pH and equilibrium time, isotherm adsorption experiments were performed. These tests included determination of the optimum dose of applied adsorbent besides the impact of initial lead concentration on adsorption process of metal ions by an adsorbent. To obtain optimum adsorbent concentration at optimum pH conditions, the obtained equilibrium time and 5 mg/L lead concentration, 200, 300, 400, 500, 700 and 900 mg/L of sorbent concentrations were assessed in 20 mL solution, respectively. Then, to determine the effect of pollution concentration, 20 mL of different concentrations 1, 2, 3, 5, 6, 7, 9 mg/L of the solution was prepared and the adsorption efficiency of lead was tested at optimum conditions pH, equilibrium time and adsorbent dosage.

In the present study, to determine the equilibrium sorption capacity of synthesized nano-sorbent, Eq. (1) was used,

$$q_e = \frac{C_0 - C_e V}{m} \tag{1}$$

where, q_e, is the amount of adsorbed metal ions per weight of adsorbent, C_0 initial concentration of lead ions in solution mg/L, C_e is equilibrium concentration of lead ions in solution mg/L, V is the volume of the solution ml, and m is adsorbent weight g.

Eq. (2) shows how to calculate the lead adsorption.

$$U_p = 100 \times \left[1 - \frac{C_e}{C_i}\right] \tag{2}$$

where, C_e and C_i are the equilibrium and initial concentrations of lead mg/L, respectively. Lead removal percentage U_p equals the amount of lead reduction after adsorbing to the initial amount of lead in the solution.

2.5. Adsorption isotherms

The correlation between the adsorbate and adsorbent amounts, at a steady temperature and optimum solution concentration, is known as an adsorption isotherm. These isotherms are used to analyze and design adsorption systems, and in addition, describe the adsorption capacity and adsorbent behavior that are important in the evaluation process [17].

In this study, Temkin, Langmuir and Freundlich adsorption isotherms were fitted to data obtained from the experiments. To determine the performance and capability of adsorbent in lead ions the adsorption from aqueous solutions, *viz*. Langmuir and Freundlich models which are more common, besides Temkin model were used. These models include the equations that are used in equilibrium condition and actually are diagrams of adsorption amount q_e and the equilibrium concentration of metal C_e.

The Langmuir model represents monolayer adsorption and homogenous surface of the sorbent. According to this pattern, an adsorbent has a uniform adsorption site with equal energy and when the process is in equilibrium state wherein the speed of molecules adsorption will be equal to their escape velocity from the adsorbent's surface [18]. Linear form of Langmuir model can be expressed as Eq. (3),

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} k_L} + \left(\frac{C_e}{q_{\max}}\right) \tag{3}$$

Freundlich isotherm model represents a multilayer adsorption on heterogeneous surfaces. Its linear equation is according to Eq. (4).