An Investigation and Comparison of Removing Heavy Metals (Lead and Chromium) from Aqueous Solutions Using Magnesium Oxide Nanoparticles

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Abstract

This study aims to investigate the efficiency of magnesium oxide nanoparticles (MON) *in vitro* for the removal of lead (II) and chromium (VI) from aqueous environments. The effects of various parameters such as contact time (15 to 280 min), pH (3, 5, 7 and 9), the initial concentration of lead/chromium (10, 20, 30.40 and 50 mg/L), absorbent dose (0.3, 0.5 and 0.8 g/L), and shaking speed (150 to 350 rpm) was investigated. The parameters were optimized by varying one parameter at a time and keeping other parameters constant. The maximum removal efficiency of MON for lead (II) and chromium (VI) was achieved at contact time 280 min, pH 9, initial concentration of lead/chromium 10 mg/L, absorbent dose 0.8 g/L, and shaking speed 250 rpm. The results also indicated that MON convert the Pb^{2+} to Pb^0 and Cr^{6+} to Cr^{3+} during the removal process. The adsorption of lead (II) and chromium (VI) follows the Langmuir isotherms, therefore the adsorption was of a physical nature.

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Introduction

The supply of healthy and safe water is one of the most important challenges for human societies, especially in developing societies. The disposal of heavy metal-rich industrial effluent without treatment to the natural water bodies is a matter of great scientific concern. Heavy metals are one of the most dangerous materials contaminating water and are very durable and irresolvable. These materials are also pathogenic and can accumulate within living organisms over time and cause disease or abnormal disorders in human health [1, 2]. Heavy metals adversely affect the body and cause many diseases and allergies [2, 3]. Heavy metals enter human or other living organisms through drinking water as well as the food chain [3, 4]. Due to the growth of industries such as electroplating, paint manufacturing, the metal smelting process and battery production, today the concentration of these metals has been high in aquatic environments [5].

Among heavy metals, lead and chromium have been mentioned as strong contaminants in the environment [6]. The most important effects of lead include disorders of the nervous and digestive systems, damage to kidneys, anemia, and damage to reproductive systems [7]. Chromium toxicity causes many chronic disorders such as dermatitis, organ damage, and respiratory impairment [8]. Heavy metals are not spontaneously wiped out in a normal state and are very stable in nature and even become more toxic and dangerous compounds over time, so they should be removed from contaminated environments using different methods. Methods such as chemical precipitation, electrochemical purification, ion exchange, osmosis, membrane process, and surface adsorption by activated carbon and industrial and agricultural residues have been extensively used for the removal of lead and chromium from water [9-12]. These methods have a few disadvantages such as chemical precipitation and electrochemical purification, do not response at low concentrations. In addition, methods of ion exchange, surface adsorption of activated carbon, and membrane processes are not cost-effective at all [5, 9, 12]. Therefore, in the selection stage of the method used for removal, these limitations should be taken into account. The adsorption process is considered one of the most safe and cost-effective processes, so the search for alternatives to activated carbon should be an area of interest for researchers [13].

In the last decade nanotechnology has been given much successful application in various fields of science but recently its utilization for the treatment of heavy metal contamination in water is a fast-growing and fascinating area of interest for the environmental scientist. Nanotechnology is a technology of preparing material in nano scale that shows unique properties such as high surface area due to their small size [14]. Many studies have been conducted using nano-materials as nano adsorbents for the removal of heavy-metal industrial effluent [5, 11].

Particle size is a relatively important feature of the particle in the adsorption of pollutants. So, the smaller the size of the particle and the higher the cross section of the

particle, the more the reactivity of these particles will be [15]. Magnesium oxide nanoparticles (MON) have such advantages as low-density, non-toxic, good ductility, and better mechanical properties compared with polymeric materials [5], large specific surface area, and high reaction level [16]. In this study, due to the electrostatic mechanism attraction and their desirable ion exchange power, the absorbent of MON was selected from other oxides [17-19]. Through studying the effects of various parameters, it has also been attempted to determine the most optimal conditions to absorb lead and chromium. The main objective of the present study was to evaluate the effects of adding MON to find a solution for the removal of lead (II) and chromium (VI) from aqueous solutions.

Experimental Activities

Raw Materials and Equipment

MONs used in the study were purchased from the Nano Pars Lima Company, while hydrochloric acid (0.1 mol/L) and Sodium Hydroxide (0.1 and 0.01 mol/L) were used to adjust solution pH, and a Metrohm pH meter device was used to measure pH values during the adsorption process. A mixer device was used for the operation of mixing penetration resistances, and mass transfer can possibly be reduced through adjusting the proper rotation. In order to separate the solid phase of absorbents from the solution, a centrifuge device with a speed of 3,000 rpm was used for centrifuging over 15 min. All analyses of lead and chromium were performed using an ICP atomic absorption device (GBC INTEGRA XL model).

In this study, the initial solutions of lead (II) and chromium (VI) were made using lead Nitrate $Pb(NO_3)_2$ and Potassium Dichromate $(K_2Cr_2O_7)$ in distilled water.

Method and Evaluation

In the present study, the absorption of lead (II) and chromium (VI) on MON was studied in a batch reactor. In the first step, stock solutions were prepared by lead nitrate salt and potassium dichromate and then it was used for preparing the desired concentrations. Next, the effect of time on the removal rate was tested. Nano-adsorbent used in this study weighed 0.8 g/L was poured in flasks with a volume of 300 ml containing 100 ml of lead Nitrate and Potassium Dichromate and after covering the mouth of the flask by paraffin film, the samples were placed on the mixer. Then, the mixing speed was adjusted to 250 rpm and the constant concentration of lead and chromium was set as 10 mg/l at 7 of pH and variable time interval of 15 to 280 min. After this time, the absorbent was separated from the adsorbed metal solution using a centrifuge device. Finally the atomic absorption device was used to analyse the amount of residual metals. The effect of some operational parameters on the removal rate of heavy metals such as pH (3, 5, 7,), initial concentration of heavy metals (10 to 50 mg/L), absorbent dose (0.3 to 0.8 g/L), and mixing

speed (150, 250, 350 rpm) was studied. However, in all of these stages, the ongoing test will be performed on the optimal values obtained in the previous stage. The amount of metal absorption was calculated according to the following calculation (Eq. 1):

$$q = v \times (C_i - C_f)/S \qquad (1)$$

...where q, C_i, C_f, v, and S are the factors of process optimization, the initial concentration of heavy metals (mg/L), the final concentration of heavy metals (mg/L), the volume of solution (l), and the amount of absorbent (g). All tests were performed at room temperature.

Isotherm Models

To study the adsorption isotherm, 0.7 g of MONs (S) were added to 1,000 mL of solution (lead and chromium solution with concentrations of 10, 20, 30, and 40 mg/L). The solutions were mixed with a speed of 240 rpm at 25ºC and pH 9. After 24 h the residual concentrations

a)

b)

Fig. 1. SEM image of magnesium oxide nanoparticles used.

of chromium and lead were measured. To describe data, Langmuir and Freundlich isotherm models were used (Eqs. 2 and 3):

$$q_e = K_f C_e^{1/n} \qquad \text{Freundlich model} \qquad (2)$$

$$q_e = q_m K_l C_e / 1 + K_l C_e \qquad \text{Langmuir model} \qquad (3)$$

...where K_f is Freundlich isotherm constant, $1/n$ is adsorption intensity, C_e equilibrium concentration (mg/L), q_e is the amount adsorbed per gram of the adsorbent (mg/g), q_m is the maximum amount of ion adsorbed on adsorbent (mg/g), and K is Langmuir constant.

Results and Discussion

MON Surface Features

In Fig. 1 (a, b), the analysis of an EM-3200 scanning electron microscope (SEM) has been assessed in order to observe and evaluate changes in the morphology and microstructures of nanoparticles. It was found that the nanoparticles are not any opening structure that have a spherical shape in the solution and the mean diameter of their particles is 20 nm and MONspecific surface is 103.5 m²/g. According to SEM analysis, it was determined that these spherical nanoparticles tend to stick to each other and form a chain state. So, MONs have a large specific surface.

Effect of Reaction Time

Results obtained in Fig. 2 show that time is one of the important factors affecting the amount of the metal adsorbed by the nano particle. Obviously, these materials
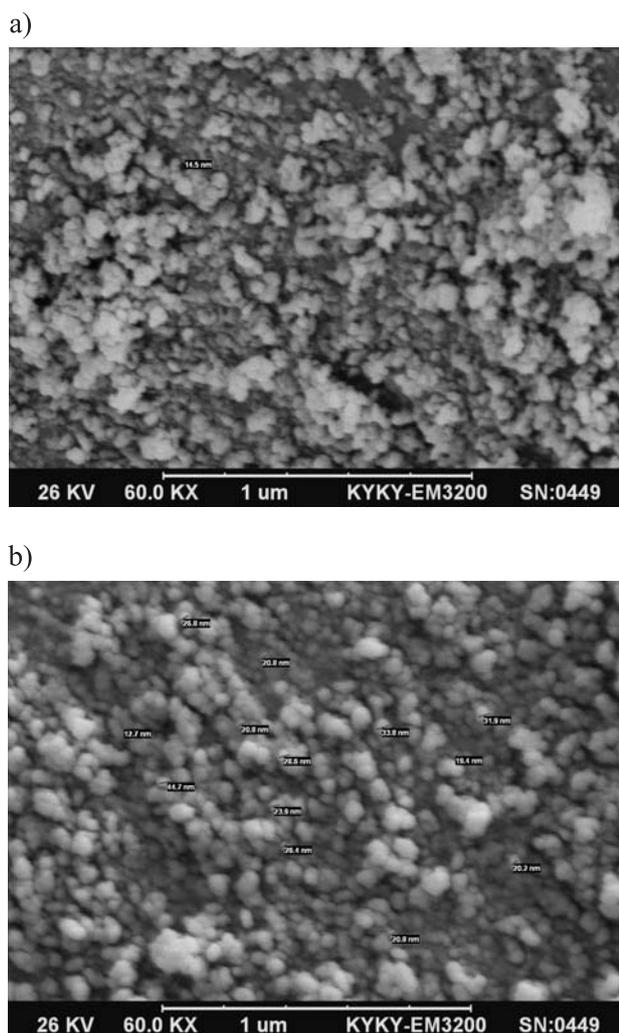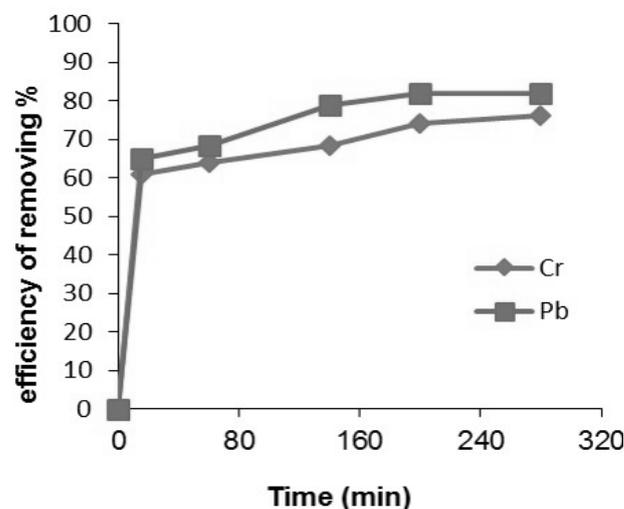

Fig. 2. Effect of contact time on the efficiency of removing lead-chromium at a concentration of 10 mg/L, fixed pH 7, absorbent dose of 0.8 g/L, and mixer rotation of 250 rpm.
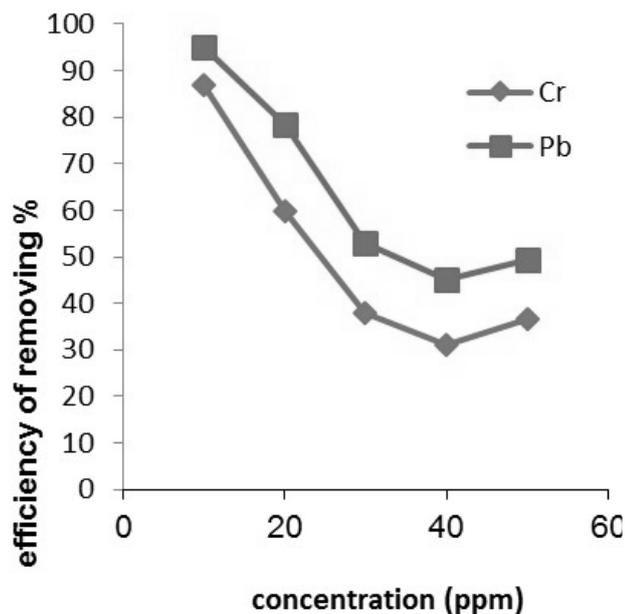
Fig. 3. The effect of initial concentration of lead-chromium (in the presence of 0.8 g absorbent, time, and optimum pH at the balance time and mixer rotation of 250 rpm).

have very large surfaces compared to other absorbents. As a result, these can remove enormous amounts of water-soluble metal. Accordingly, in this study short time intervals were selected for obtaining optimal conditions. Results showed that the removal efficiency of lead-chromium increased over time.

As can be observed in Fig. 3, the results of this stage could be divided into two parts: in the first part, the removal efficiency of lead-chromium increased rapidly during a short time (between 0 to 15 min). Then a significant increase was achieved in the time interval of 15 to 280 min. This result can be attributed to the large difference between concentrations of lead, water-soluble chromium, and lead-chromium in absorbent that has a very great desire to move quickly toward absorbent and to be absorbed on it. At the beginning of the process, lead and chromium were quickly removed by the absorbent. Having a large number of free sites on the adsorbent surfaces at the beginning of the reactions was another reason for quick absorption. In other words, the less-saturating active sites on the absorbent lead to an increase in the speed of collision between metal ions and adsorption sites [20, 21]. On the other hand, in the second part the removal rate of lead-chromium increased with a very low speed in the range 15 to 280 min. This increase can be related to the created environment conditions in the solution. In fact, by creating such conditions, ions of lead-chromium find an opportunity to move very slowly toward the absorbent as a result of the concentration difference between the solution and absorbent. Results of another study conducted by Heidari et al. on lead removal from aqueous solution using the modified MCM-41 Nano-pore absorbent confirm our results [22].

Effect of pH

Solution pH is one of the important factors affecting the area properties and area load of absorbent in the absorbent process. The obtained results show that adsorbent efficiencies at pH values of 3, 5, 7, and 9 were 2.7, 63, 49, 73, and 81.25%, respectively, for chromium removal, while they were 2.25, 5.53, 2.67, and 94.78% for lead removal (under similar conditions: 0.8 of adsorbent, 10 mg/L of metal concentration, mixing speed of 250 rpm and 280 min of reaction time). Based on the obtained results the removal rate of lead and chromium increased with increasing pH values. The maximum adsorption capacity of lead and chromium was observed for MON at pH = 9. This is due to the fact that at high pH values, MON is justified because of decreasing H^+ in the water environment, increasing OH^- and negative anions on the absorbent surface.

At high pH values metal nitrates will have positive loads in aqueous solutions, which can lead to an increase in absorbent efficiency. Results of other studies are consistent with findings of the present study [15, 23]; in a similar study on the MON efficacy in the treatment of industrial wastewater, Mousavi et al. reported that the maximum removal efficiency was obtained at pH 8.5 [17]. Also, in the study conducted by Shokohi et al. on the removal of heavy metals from aqueous solutions using modified aerogel, results showed that the removal rate of lead increased with increasing pH values [23].

Effect of Metal Initial Concentration

To evaluate the effects of initial concentration of chromium we tested five concentrations of 10, 20, 30, 40, and 50 mg/L. In MON, the removal efficiency reduced with increasing concentrations, in which the maximum removal of the metals was obtained at concentrations of 10 mg/L. This can be attributed to the decrease in the thrust force (intermolecular forces) and possibly to the low solubility of nano-adsorbent in high concentrations of metal solution. By increasing NOM concentration, its solubility decreased. This can be attributed to high concentrations of metals, and as a result, removal efficiency decreased (Fig. 3).

Effect of the Adsorbent Dose

To evaluate the effect of the initial value of adsorbents on the removal efficiency of metals, the rate of adsorbent rotation was tested in three rates of 0.3, 0.5, and 0.8 g/L. Based on the observed results, by increasing the concentration of adsorbent in solutions the removal rate of chromium and lead increased significantly. This increase in the removal process can be attributed to the increase in the specific area and probability of collision between particles of adsorbent and ions of metal. The results of other studies are also relatively consistent with these results.

A similar study conducted by Shahbazi et al. showed that the rate of removing metal increased while increasing the adsorbent rate [24]. Also, in another study conducted
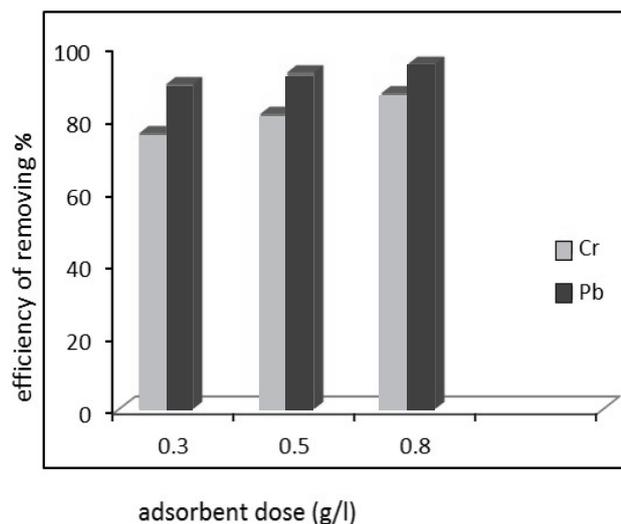
Fig. 4. The effect of the rate of adsorbent dose (in the presence of optimal time and pH, optimal concentration, and mixer rotation of 250 rpm).

Table 1. The parameters obtained from both studied models (Freundlich and Langmuir).

Freundlich			Langmuir			Adsor-bate
K_f	n	R^2	q_m	K_l	R^2	
11.857	9.93	0.88	16.44	1.88	0.96	Cr^+
1.286	1.53	0.925	21.78	0.0373	0.96	Pb^+

by Rahmani et al., results showed that by increasing the adsorbent, the rate of metal removal increased [25]. Results show that the removal efficiency of metals was related to the increase in the adsorbent amount. It should be noted that in the adsorption process, the increase of adsorbent dosage has serious limitations such as improper functioning of devices, high adsorbent requirements, increased sludge production, and high costs associated with purchasing absorbent. Therefore, by increasing adsorbent amount, the total cost of the process should also be considered. Moreover, it cannot be certainly said that in all cases is the process economically the best process proposed for removing chromium and lead from water. Because the determination of the best process is influenced by several factors, not one factor. Some limitations including observed environmental standards, being economical process, availability of materials, and absorbents and some other cases should be considered.

Effect of Mixing Speed

To evaluate the effect of mixing speed on the adsorption efficiency in removal of studied metals, experiments was done in three mixing speeds of 150, 250 and 350 rpm. Results indicated that the removal efficiency of chromium in the mentioned range of mixing speed was 58.25, 81.2 and 64.5%, respectively. Moreover, the removal efficiency of lead in the mentioned range of mixing speed was 72.2, 94.25, and 81%. Therefore, the maximum process efficiency was obtained at 250 rpm of mixing speed. Furthermore, it can be said that the optimum value of mixing speed could lead to an increase in the number of contacts between adsorbent and adsorbed metals.

However, by increasing mixing speed higher than 250 rpm in the solution, removal efficiency decreased. This phenomenon can be attributed to the fact that in an adsorption process at high mixing speeds, some of the adsorbed metals are removed from the adsorbent surface. On the other hand, in the process at low mixing speeds, the metal ions have a very low speed to adsorb onto the adsorbent sites. As a result, in the adsorption process adsorption efficiency decreased at low mixing speed values.

Effect of Isotherm Models on Lead and Chromium Adsorption

Table 1 shows the results of isotherm studies. The isotherm data were fitted well with the Langmuir model with higher correlation coefficient (R), which indicated that lead and chromium were physically adsorbed on the adsorbent surface. In physical adsorption, the adsorbate molecules are adsorbed on the surface of absorbent particles as a layer. In Langmuir model the absorbent capacity for adsorbing lead and chromium were 16.44 and 21.78 mg/g, respectively.

Conclusion

Lead and chromium are the most important environmental pollutants and major factors threatening human and environmental hygiene. Results determined that MONs have high capacity as an adsorbent for removing lead and chromium. Obtained results showed that the reaction was done at a wide range of pH and the highest removal efficiency was obtained at base pH. The obtained results indicated that the percentage removal of lead is higher than that of chromium. In general, it can be concluded that MONs will be used as a useful, simple, and fast method with high performance for removing lead and chromium from industrial wastewaters in water and wastewater plants. Because of the importance of separating this metal from wastewaters, our study results can also be considered a new approach in the field.

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