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Study of Cadmium and Nickel Removal from Battery Industry Wastewater by Fe_2O_3 Nanoparticles

Shahriari, T.*, Mehrdadi, N. and Tahmasebi, M.

School of Environment, College of Engineering, University of Tehran, Tehran, Iran

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ABSTRACT: Nickel and cadmium usually enter the environment and water resources through wastewater, released by various industries, and may have adverse effects. The current study employs α–Fe_2O_3 nanoparticles of 20-40 nm in order to remove nickel and cadmium from the wastewater of Saba Battery Company. Also, it investigates the influence of effective parameters on adsorption process, including pH, contact time, and the adsorbent rate so that it can optimize the adsorption process. The maximum adsorption rate of nickel and cadmium can be observed in pH ranges of 5 to 9. In addition, adsorption rates for nickel (at pH = 7) and for cadmium (at pH = 5) have been 92.98% and 93.97%, respectively. By increasing the adsorbent rate, the adsorption grows, due to the increase in absorbate surface area, and an optimum adsorbent rates of 0.15 g and 0.2 g are obtained for cadmium and nickel, respectively. The maximum nickel and cadmium adsorption rates occur during the first 60 min of contact with nanoparticles. In this study, adsorption kinetics and isotherms have also been investigated and it has been found that the adsorption kinetics of both nickel and cadmium ions follow the pseudo-second-order model, while adsorption isotherms of nickel and cadmium follow the Freundlich model.

Keywords: Adsorption Isotherms, Adsorption Kinetics, Battery Industry, Heavy Metals.

INTRODUCTION

Nowadays, one of the most important issues all around the world is the environmental pollution created by toxic and dangerous heavy metals. Industrial wastewater that enter waters is one of the most prominent sources of pollutions, with nickel and cadmium being two prominent examples in this phenomenon. Discharged by various industrial units like battery industry and in different rates to waters, the compounds of these elements have adverse effects on most vital ecosystems, entering human food chain in various ways. The entry of these compounds into human body is cancerous, causing lung, kidney, heart, and bone diseases as well (Coman et al., 2013; Zavvar Mousavi and Seyedi, 2011; Chergui et al., 2014; Iqbal et al., 2007). In recent year, the need for refining and reuse the metal ions prior to industrial wastewater release into the environment has attracted the attention of some researchers with an environmental point of view (Pyrzynska and Bystrzejewski, 2010; Gupta and Nayak, 2012).

For example, Hu et al. (2005) dealt with the recovery and removal of chromium from wastewater, using magnetic iron oxide nanoparticles. Dermentzis et al. (2012) studied simultaneous removal of acidity and lead from wastewater released

* Corresponding Author, E-mail: Tshshahriari@ut.ac.ir

by battery industry, using electro-coagulation. Bahadir et al. (2007) investigated the removal of lead from battery industry, using biologic adsorption. Elouear et al. (2009) performed the removal of nickel and cadmium from aqueous solutions by means of Sewage Sludge Ash.

Conventional methods for removal of heavy metals are based on physical and chemical techniques, which include filtration, chemical precipitation, ion exchange, nanotechnology, etc. (Ahluwalia and Goyal, 2007; Alarcon-Payan et al., 2017; Amen et al., 2018; Behboudi et al., 2018; Jadhav and Biswas, 2018; Pouretedal, 2018; Rostami and Joodaki, 2002; Shahriari et al., 2014; Shen et al., 2009; Sheng et al., 2018; Vilardi et al., 2018). Thanks to a number of properties of adsorption process, such as selective adsorption capacity of metal ions, adsorption in very low metal concentrations, high adsorption capacity due to high specific surface area, absence of secondary toxic compounds, possibility of adsorbed metals' desorption, and reuse of adsorbents, this method becomes a novel one, which must be the present study's priority (Azadi et al., 2018; Eskandari et al., 2019; Liu et al., 2019; Shen et al., 2009; Wang et al., 2018). The main objective of this study is, therefore, to provide a method for adsorption of nickel and cadmium ions in wastewater by means of iron magnetic nanoparticles and to obtain optimal parameters of this method.

MATERIALS AND METHODS

The study conducted its experiments on the wastewater from Saba Battery industry Co., located in Shahriar city (Tehran, Iran). The average nickel and cadmium concentrations in the wastewater samples were about 4.13 and 0.83 mg/L, respectively. Nanoparticles of α-Fe_2O_3 with a purity of 98%, diameter of 20-40 nm, true density of 5.24 g/cm^3, and spherical morphology were purchased from Pishgaman Iranian Nanomaterials Company.

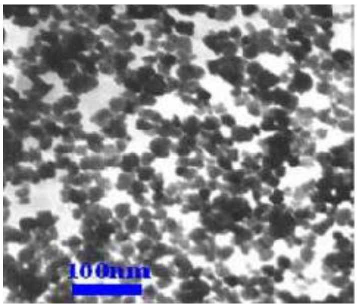

Fig. 1. The transmission electron microscopy of the magnetic nanoparticle α-Fe_2O_3 (TEM)

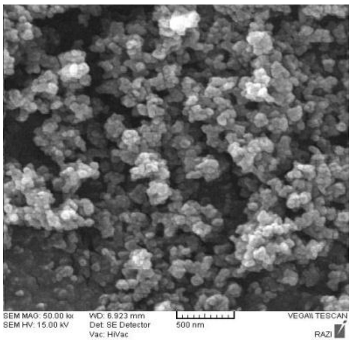

Fig. 2. The scanning electron microscopy of the magnetic nanoparticle α-Fe_2O_3 (SEM)

In order to carry out the experiments, the study made use of METTLER digital scale (AE2000 model), an oven made by Fan Azma Goster (BF400E), a Swiss-made 691 pH Meter-Metrohm, and IKA® Orbital Shaker KS 501 digital. Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were used to adjust the pH and the samples were transferred in 100-ml polyethylene containers for the purpose of measurement.

For optimizing the adsorption process, the pH of the solution was first measured in the constant adsorbent rate and time, at 25°C, with an agitation rate of 200 rpm. Once the pH got determined, the adsorption tests were carried out in different absorbent doses, with the optimum time obtained via changing the time. The experiments were performed three times so that the tests' validity could be confirmed.

RESULTS AND DISCUSSIONS

In order to determine the effect of pH on adsorption process, the pH was set at 1 N, by means of sulfuric acid and sodium hydroxide. The solutions were placed on a shaker with an agitation rate of 200 rpm for 60 min. After obtaining the residual concentration and calculating the equilibrium adsorption capacity and removal percentage, the appropriate pH value got selected.

Figure 3 illustrates the schematic view of pH effect on nickel adsorption, showing that by increasing the pH from 3 to 7, the adsorption rate rose with a relatively large gradient, reaching 92.98%. As can be seen in this figure, the maximum removal was observed at a pH rate of about 9, but due to environmental considerations, a pH rate equal to 7 was taken into consideration for pH-removal experiments. In order to determine the optimum value of other parameters, the experiments, pertaining to Nickel removal, took place with pH = 7.

Figure 4 shows the schematic view of pH effect on cadmium adsorption. In addition, it demonstrates that by increasing pH from 3 to 5, the adsorption rate rose with a relatively high gradient, reaching 97.93%.

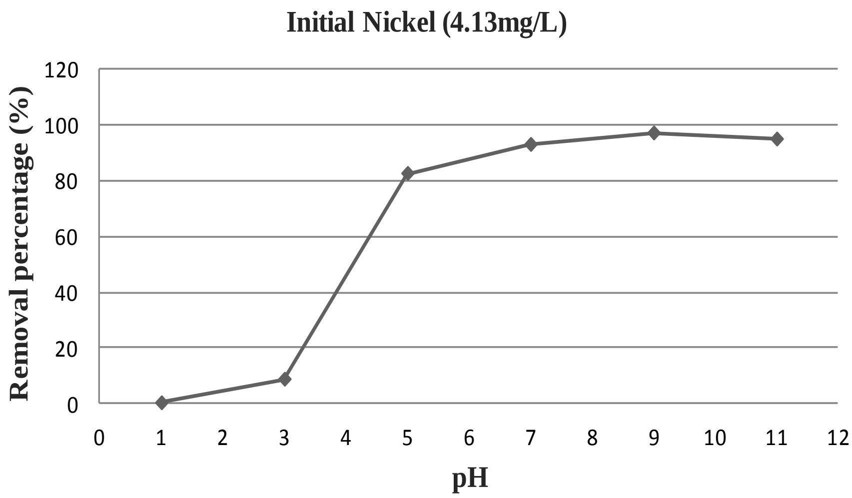

Fig. 3. The effect of pH on nickel adsorption via magnetic α-Fe_2O_3 nanoparticle

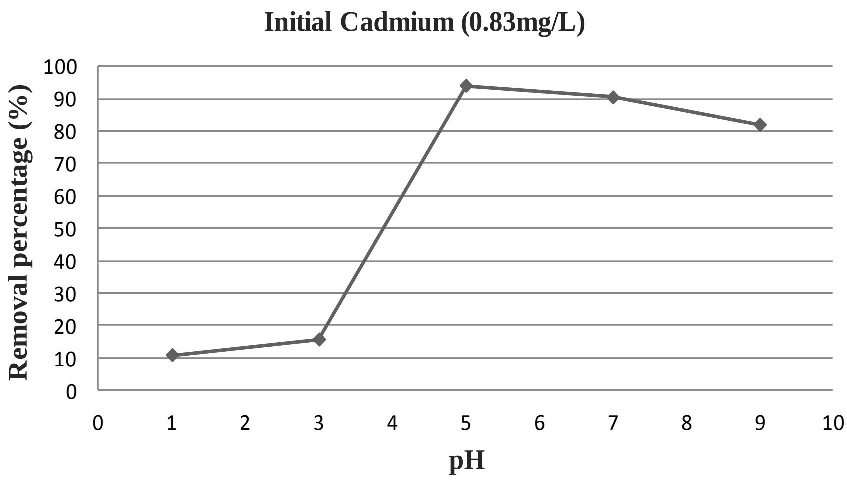

Fig. 4. the impact of pH on cadmium adsorption via magnetic α-Fe_2O_3 nanoparticles

According to Figures 3 and 4, by increasing the pH, adsorption sites got a negative charge by hydroxide ions, which increased the electrostatic force between the adsorbent surface area and nickel and cadmium ions; therefore, the adsorption rate was increased. By decreasing the pH, the adsorbent hydroxide surface got weakened, leading to a decrease in these metal ions' adsorption. The experiments in this study showed that the appropriate pH for removal of cadmium by magnetic α-Fe_2O_3 nanoparticles was about 5. Shen et al. (2009) showed that in pH rates greater than 4, the nickel and cadmium metal ions got adsorbed by Fe_3O_4 magnetic nanoparticles. Also, investigation of the cadmium adsorption by Chen et al. (2011) showed that the appropriate pH for cadmium adsorption was between 3 and 6. Onundi et al. (2011) studied the adsorption process and concluded that the suitable pH for heavy metal adsorption (lead, copper, and nickel) was equal to 5 (Onundi et al., 2011).

In order to investigate the effect from changes of adsorbent rate on adsorption process, a solution containing nickel and cadmium in contact with nanoparticles of α-Fe_2O_3 was prepared. For this purpose, pH values was considered 7 for nickel and 5 for cadmium. The solutions were then placed on a shaker at 200 rpm for 60 min. After obtaining the residual concentration and calculating the equilibrium adsorption capacity and removal percentage, the appropriate adsorbent rate was selected.

Figure 5 shows the changes of nickel adsorption against the ones in the mass ratio of α-Fe_2O_3 nanoparticles. As can be observed, by raising the nanoparticle levels, the adsorption increased, which was due to the increase of free sites on the surface of the nanoparticles.

Results showed that the rate of nickel adsorption with nanoparticle level of 0.4 g in 100 cc wastewater was 96% and for nanoparticle level of 0.2 g in 100 cc wastewater, 92.99%. Considering the results, the experiments were carried out at a constant rate of 0.2 g to find other optimal parameters.

Figure 6 demonstrates the rate of cadmium adsorption against the changes in the amount of α-Fe_2O_3 nanoparticles.

It can be concluded that the best adsorption occurred in the nanoparticle level of 0.15 g in 100 cc of wastewater. Therefore, in order to find other optimal parameters, the experiments were continued at a constant rate of 0.15 g.

The results, presented in this figure, show that by raising the nanoparticle levels, the removal rate increased, too. In addition, it can be seen that the higher the nanoparticle levels, the greater the adsorption sites; thus, the removal percentage of nickel and cadmium from wastewater rose, too. Shen et al. (2009) and Nosier (2003) concluded that an increase in nanoparticle levels may increase the removal efficiency of the pollutants.

In order to fully determine the impact of time on adsorption process, the research considered periods of 20, 40, 60, 80, and 100 min. The experiments were carried out for nickel ion with 0.2 g of nanoparticles and at pH of 7. For cadmium ion, this was 0.15 g of nanoparticles at pH of 5. After performing the tests, the appropriate time was chosen. Figure 7 shows the amount of nickel adsorption in terms of time. As can be seen for a period of 60 min, the adsorption process almost reached equilibrium. In addition, Figure 8 shows the adsorption rate of cadmium.

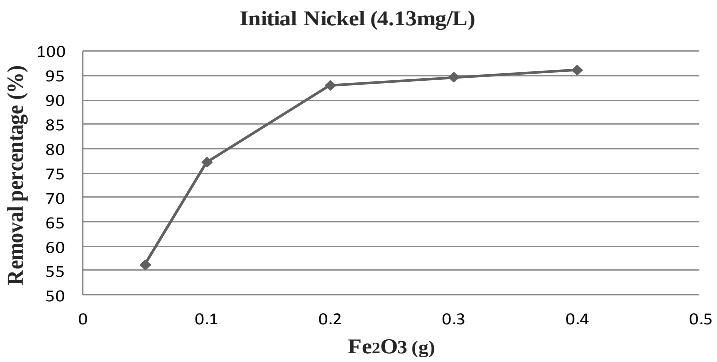

Fig. 5. Effect of α-Fe_2O_3 nanoparticle amounts on nickel adsorption

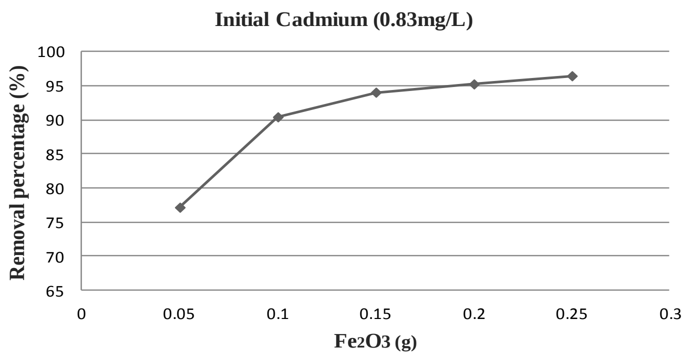

Fig. 6. Effect of amounts of α-Fe_2O_3 nanoparticle on cadmium adsorption

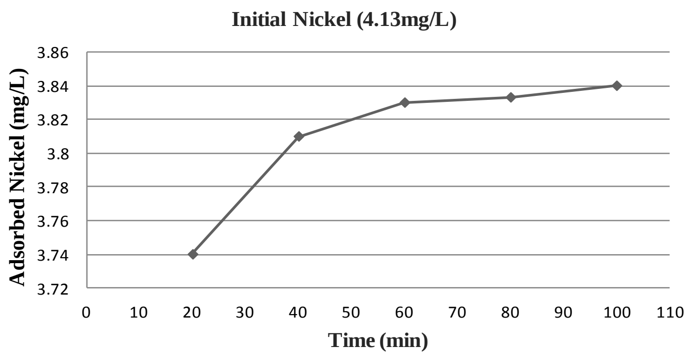

Fig. 7. Effect of time on nickel adsorption via magnetic α-Fe_2O_3 nanoparticles

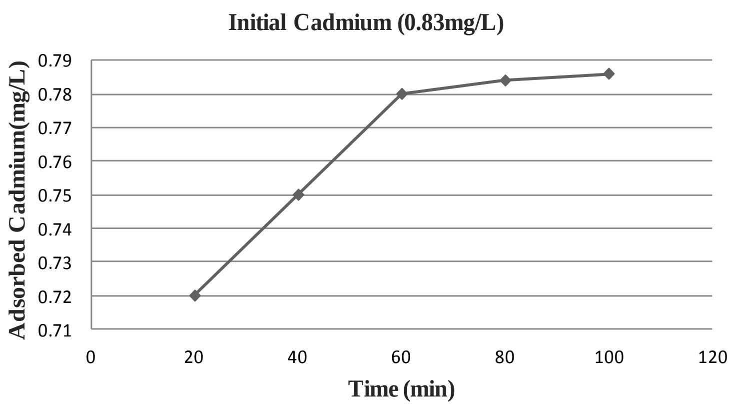

Fig. 8. Effect of time on cadmium adsorption via magnetic α-Fe_2O_3 nanoparticles

As can be seen, the removal rate was about 93.97% for the time period of 60 min. It should be noted that increasing the duration of the tests increased the removal rate, although this would continue until adsorption sites were saturated. Thereafter, no adsorption would take place as a result of increasing the time. Shen et al. (2009) and Nosier (2003) showed that as the test time increased, the adsorption rate rose. Absorption of cadmium was considered to take 20 min. Figures 9 and 10 show, respectively, the first and second order adsorption kinetics of nickel ion.

Figures 11 and 12 respectively show the first and second order adsorption kinetics of cadmium ion.

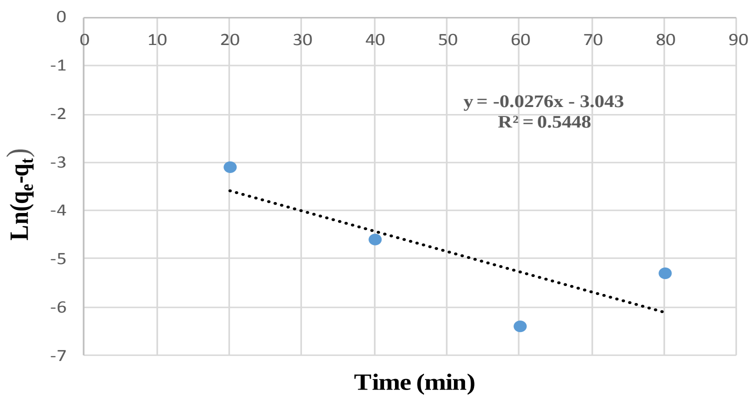

Fig. 9. Pseudo-first-order equation curve for nickel adsorption via α-Fe_2O_3 nanoparticles

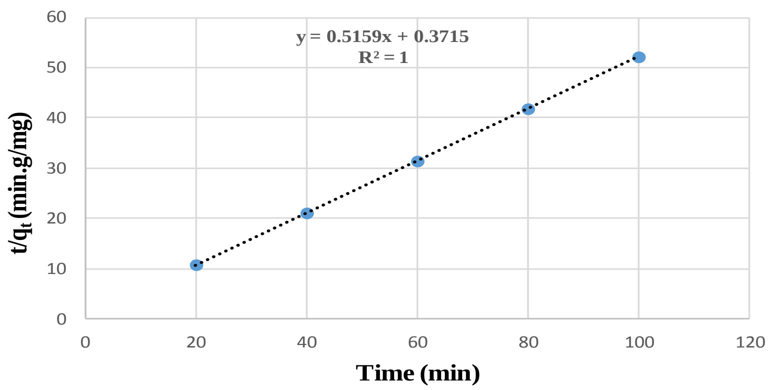

Fig. 10. Pseudo-second order equation curve for nickel adsorption via α-Fe_2O_3 nanoparticles

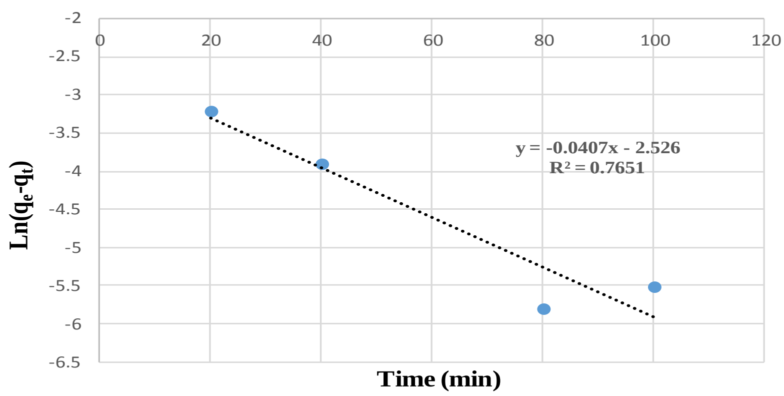

Fig. 11. Pseudo-first-order equation curve for cadmium adsorption via α-Fe_2O_3 nanoparticles

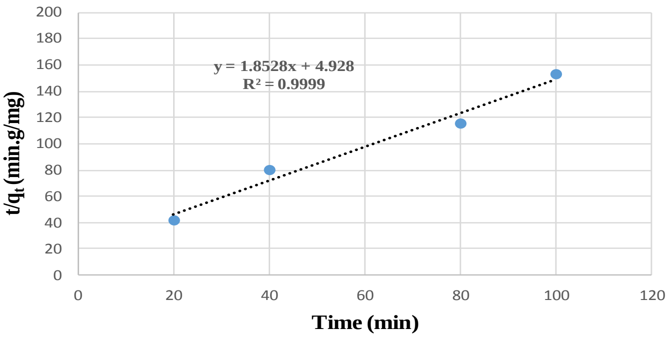

Fig. 12. Pseudo-second-order equation curve for cadmium adsorption via α-Fe_2O_3 nanoparticles

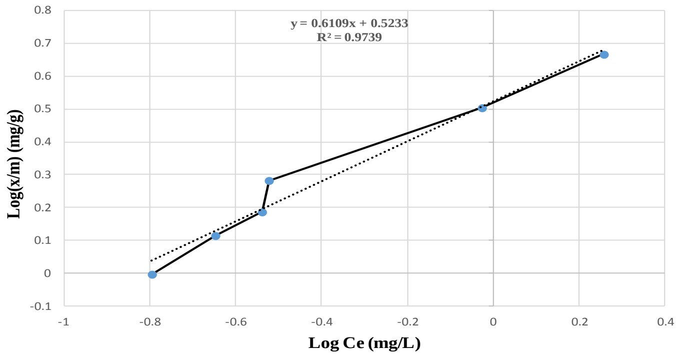

Fig. 13. Freundlich isotherm of nickel adsorption via α-Fe_2O_3 nanoparticles

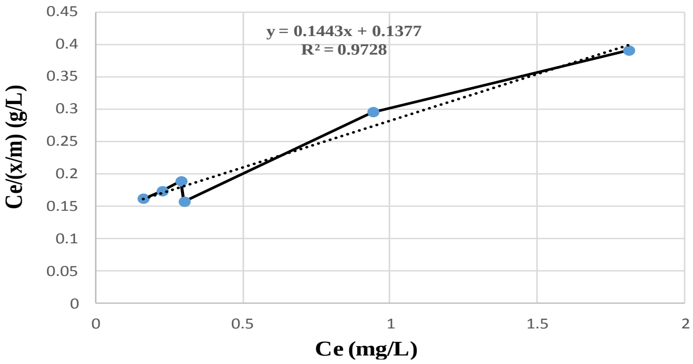

Fig. 14. Langmuir isotherm of nickel adsorption via α-Fe_2O_3 nanoparticles

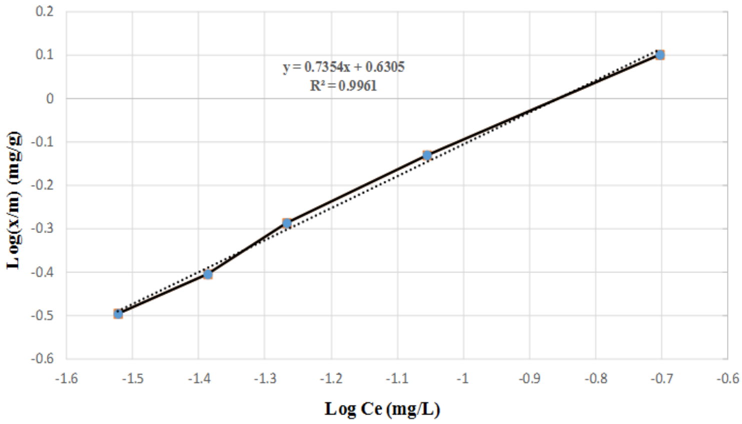

Fig. 15. Freundlich isotherm for cadmium adsorption via α-Fe_2O_3 nanoparticles

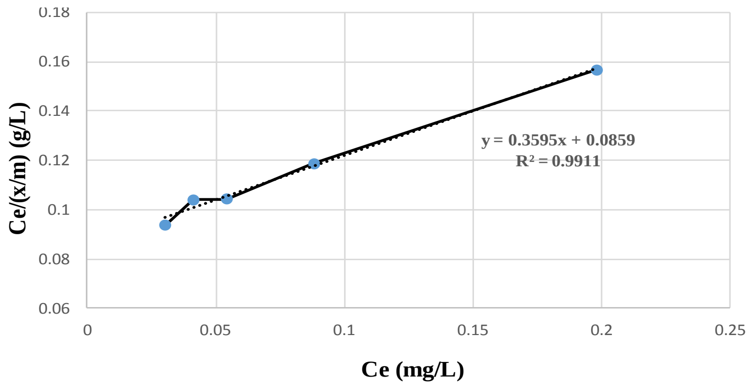

Fig. 16. Langmuir isotherm for cadmium adsorption via α-Fe_2O_3 nanoparticles

By comparing the data and diagrams of nickel and cadmium adsorption profiles, it can be concluded that adsorption kinetics followed the pseudo-second-order model. In addition, the pseudo-second-order model indicated that adsorption depended on the adsorbed and absorbent. Mohammad et al. (2010) studied the removal of metal ions from aqueous solutions and introduced pseudo-second-order kinetics model.

In order to investigate the mechanism of nickel and cadmium adsorptions by iron magnetic nanoparticles, the Langmuir and Freundlich isotherm constants were fitted to the data. The amount of absorbed ions per unit mass of the absorbent is a function of the soluble material's concentration. Investigating these two quantities at a constant temperature determines the adsorption isotherms. In this study, these two models were used to plot adsorption data.

As can be seen, Langmuir and Freundlich isotherms were the models, used to evaluate nickel and cadmium adsorption on magnetic iron nanoparticles. Considering the above figures and values of R^2, it can be concluded that Freundlich isotherm was a more suitable model for nickel and cadmium adsorptions on iron oxide nanoparticles. It shows that the adsorption sites had different energies. Hu et al. (2005) introduced Freundlich adsorption isotherm for removal and remediation of chromium from wastewater via magnetic nanoparticles. Finally, having investigated the removal of arsenic (III) from groundwater by zero-valent iron nanoparticles, Kanel et al. (2005) found that adsorption isotherm followed the Freundlich model as well.

CONCLUSION

There are several methods to remove heavy metals from wastewater. The present study investigated the removal of nickel and cadmium from wastewater of battery industry via magnetic iron oxide nanoparticle. The results showed that by increasing the pH, the adsorption rate rose, too. It should be noted that in high pH values, the amount of hydroxide ion was increased, leading to the formation of metal ion precipitation. By increasing the adsorbent rate, the adsorption rate rose due to the increment in adsorbate surface area, which also resulted in an optimum adsorbent dose of 0.15 g for cadmium and an adsorbent dose of 0.2 g for nickel. As the contact time increased, more pollutants got absorbed into the active surface of the nanoparticles, with the maximum adsorption rates for nickel and cadmium solutions occurring during the first 60 min of contact with nanoparticles. The adsorption kinetics of both nickel and cadmium metal ions followed a pseudo-second-order model. In Freundlich isotherm the adsorption occurred on the heterogeneous surfaces, while Langmuir isotherm showed the adsorption was uni-layered with adsorption occurring on homogeneous surfaces. In the current study, nickel and cadmium adsorption isotherms followed Freundlich model.

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