Competitive adsorption of Ni^{2+} and Cd^{2+} on the PAN/SiO_2 composite nanofiber adsorbent

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Abstract
In this study, PAN/SiO_2 composite nanofiber adsorbent was prepared by the electrospinning method and characterized by SEM. The SEM image showed that the nanofiber adsorbent was formed in average diameter of 370 nm. After all, the prepared adsorbent was applied in competitive adsorption of Ni^{2+} and Cd^{2+} at various initial concentrations within the range of 30 to 500 mg L^{-1} for each metal ions. Consequently, it was observed that Ni^{2+} adsorption was more affected in the presence of Cd^{2+} in comparsion with inhabitory effect of Ni^{2+} on the Cd^{2+} adsorption. Also, the adsorption affinity of metal ions was in order of $Cd^{2+}>Ni^{2+}$ and the maximum adsorption capacity of Cd^{2+} and Ni^{2+} were 92 and 31 mg g^{-1} respectively.

Keywords: Adsorption, Cd^{2+}, Ni^{2+},Nanofibers, SiO_2

1. Introduction
Nowadays, the industrial treatments of wastewaters containing a trace amount of heavy metals are regarded as a serious environmental concern [1]. heavy metals could accumulate through food chain relationships and lead to serious diseases such as lung insufficiency, bone lesions, cancer, carcinogen and birth defects in humans [2-4]. Among them, Ni^{2+} and Cd^{2+} are encountered in raw wastewater streams from industries such as non-ferrous metal production, mineral processing, metallurgical alloying, electroplating, textile, ceramics, porcelain enameling, steam-electric power plants and batteries [5]. So, reduction of this hazardous contamination to standard level is very important.
Among the conventional methods for heavy metal removal, adsorption has been extensively used because it is economically feasible, effective, simple and environmentally appropriate in practice [6-8]. In this study, the polyacrylonitrile (PAN)/SiO_2 adsorbent was prerared by electrospinning process. Then, the competitive adsorption of Ni^{2+} and Cd^{2+} on the PAN/SiO_2 composite nanofibers were investigated. Also, the surface of the adsorbent characterized by SEM.

2. Experimental
2.1. Materials

PAN (MW = 150,000), SiO_2 nanoparticles (diameter = 7-25 nm), N, N-Dimethylformamide (DMF), HCl, HNO_3 and NaOH were purchased from Merck. The solutions of Cd^{2+} and Ni^{2+} were prepared by dissolving the weighed amounts of metal salt in deionized water.

2.2. Equipments

The concentrations of Cd^{2+} and Ni^{2+} in the solutions were determined by an inductivity coupled plasma atomic emission spectrophotometer (ICP-AES, Thermo Jarrel Ash, Model Trace Scan).Also, the morphological analyses of the adsorbent was characterized using a scanning electron microscope (SEM, JEOL JSM-6380).

2.3. Preparation of adsorbent

The PAN solution was prepared by slowly dissolving 8 g of PAN in 100 mL DMF at an ambient temperature and stired for 30 hr.Then, PAN/SiO2 composite nanofiber was prepared adding the 1.6 g SiO_2 nanoparticles in the PAN solution very slowly and stirring it for 1 hr. For homogenous dispersion of the nanoparticles in the PAN solutions, the solutions was placed in the ultrasound device (Model: DSA 100-SK2-4.0 L) for 30 min. Finaly, the solutions were converted to composite nanofibers by the electrospinning apparatus.

3. Results and Discussion

3.1. Characterization

The SEM image of the adsorbent showed that the nanofibers were formed after electrospinning process. As can be seen from fig. 1, beads are seen on the surface of PAN/SiO_2 nanofibers due to aggregation of nanoparticles in the polymer solution. Furthermore, incorporation of silica nanoparticles affected the surface shape of the fibers. As a result, the average diameter (AD) of nanofibers calculated by ImageJ program and it was 370 nm.

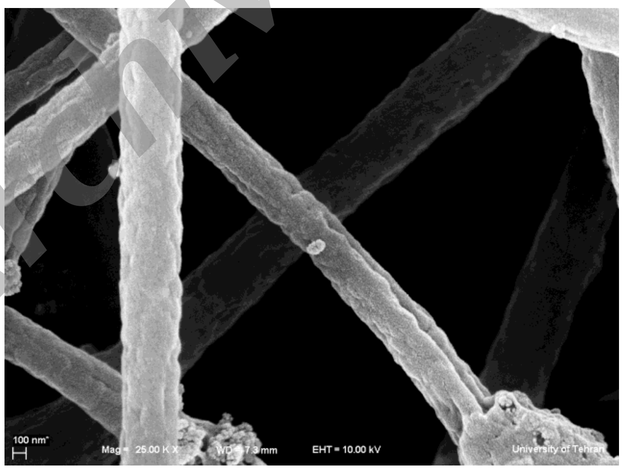

Fig. 1. The SEM image of PAN/SiO_2 composite nanofiber adsorbent

3.2. Adsorption

The binary solutions of Ni^{2+}–Cd^{2+} ions were applied to investigate the inhibitory effects of these ions on the adsorption capacity of each other. Adsorption experiments were carried out by the batch method in a 200 mL flask by adding 0.1 g of the adsorbent in 100 mL of metal solutions at 45 °C. The initial pH of the solutions were adjusted with 0.1 M HCl and/or 0.1 M NaOH solutions. As a significant parameter, the optimum pH for adsorption process was selected pH 6 due to results reported in Irani et. al work [9]. In order to consider the effect of the initial concentration of the metals, the equilibrium adsorption of each metal ions at initial concentration in the range of 30-500 mg L^{-1} and in the presence of other metal ions in various concentrations (30-500 mg L^{-1}), was examined. As shown in figs. 2 and 3, it was detected that the presence of Cd^{2+} ions more affected the adsorption of Ni^{2+} ions rather than that of Ni^{2+} ions in Cd^{2+} containing solution. On the other hand, by increasing Cd^{2+} concentration from 30 to 500 mg L^{-1} in the binary adsorption, Ni^{2+} adsorption reduced from 31 mg g^{-1} to 19 mg g^{-1}. Besides, the adsorption capacity of Cd^{2+} reduced from 92 to 57 mg g^{-1} in the increasing concentration of Ni^{2+} from 30 to 500 mg L^{-1}. These results showed that the parameter such as electronegativity of the metal ions, hydroxo complex formation abilities and preferred adsorption sites on the adsorbent had significant effect on the adsorption process. The adsorption affinity of the adsorbent for Ni^{2+} and Cd^{2+} ions in the binary systems was in order of Cd^{2+}>Ni^{2+}.

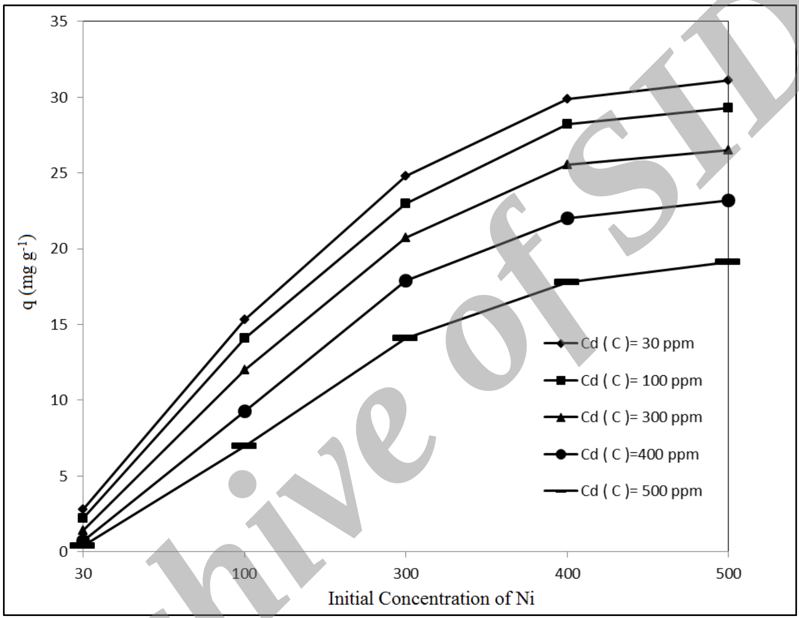

Fig. 2. Effect of Cd ions on the adsorption of Ni ions onto the adsorbent

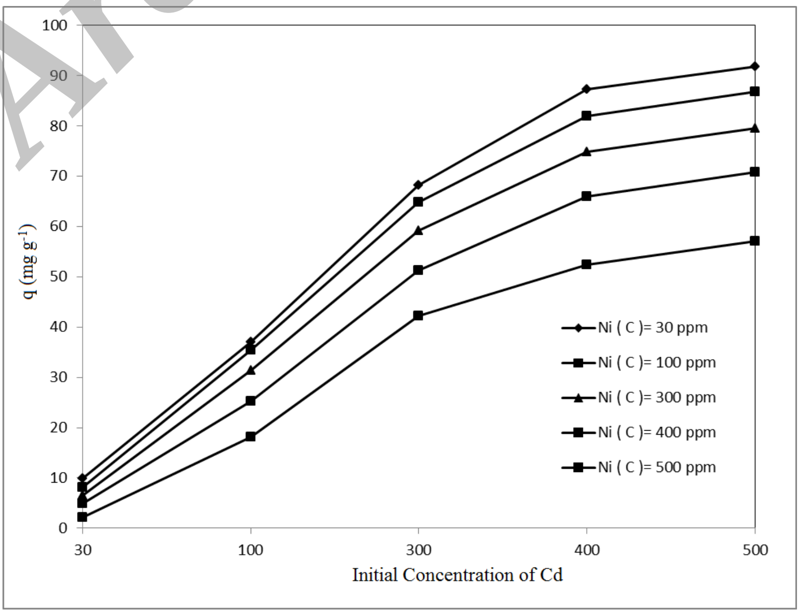

Fig. 3. Effect of Ni ions on the adsorption of Cd ions onto the adsorbent

4. Conclusions

In this study, PAN/SiO_2 composite nanofiber adsorbent was prepared by the electrospinning method to examine the removal of Cd^{2+} and Ni^{2+} ions from aqueous solutions, characterized by SEM image. From the binary adsorption data, it was concluded that the adsorbent presented greater affinity for Cd^{2+} compared with Ni^{2+}. Also, it was observed that the presence of Cd^{2+} ions greatly affected the adsorption of Ni^{2+} ions rather than the presence of Ni^{2+} ions in Cd^{2+} containing solution. Furthermore, both metals adsorption capacity was in the maximum level when the other was in the lower concentration

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