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ORIGINAL PAPER

Adsorption of cadmium and nickel from aqueous environments using a dendrimer

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ABSTRACT

Numerous heavy metals such ascadmium and nickel are toxic present in industrial wastewater and could cause severe damage to living organisms. These compounds are considered to be common contaminants, which are discharged into water resources and cause major environmental problems. Due to the excessive toxicity of heavy metals even at low concentrations, they also threaten human health. Therefore, it is essential to remove these elements from wastewater before discharge into the environment. The present study aimed to evaluate the adsorption of cadmium and nickel from aqueous solutions using poly (propyleneimine) (PPI) dendrimer, as well as the influential factors such as pH, PPI dosage, and the initial concentration of cadmium and nickel using a batch model. To assess the mechanism of adsorption and calculate the maximum adsorption values, the Langmuir and Freundlich isotherms were used. The findings indicated that increased pH and adsorbent dosage improved the removal efficiency. In contrast, increased heavy metal ion concentrations decreased the adsorption. According to the dynamic light scattering analysis, the mean diameter of the PPI dendrimer was 1-10 nm, and the maximum adsorption of both heavy metal ions occurred at the pH of seven. In addition, the maximum uptake of cadmium and nickel was attained with the adsorbent dosage of 0.08 g/L. The maximum removal capacities of the PPI dendrimer for nickel and cadmium were estimated at 1,428 and 1,225 mg/g, respectively.

Keywords: Adsorption, Cadmium, Nickel, Dendrimer

Introduction

Heavy metals are important water pollutants (particularly in industrial areas), which have led to significant issues in recent years.[1] Since heavy metals are toxic, resistant, non-biodegradable, and agglomerative within environmental systems, they pose a significant risk to humans and other organisms even at low concentrations.[2-4] Therefore, the removal of heavy metals from aquatic systems has greatly attracted the attention of researchers.[5-7]

Several techniques have been proposed for the uptake of heavy metal ions fromaquatic systems, including chemical precipitation, solvent extraction, ion exchange, and adsorption.[8-10] Among these technologies, adsorption is considered to be most effective.[11] The major superiority of adsorption is that adsorbents have potent affinity and great capacity for heavy metal removal.[12] In recent years, poly (amidoamine) and poly(propyleneimine) (PPI) dendrimers are extensively applied in environmental operations.[13,14] PPI dendrimers have the preponderance of spherical geometry with high amino functional groups and high aggregation of nitrogen atoms, which could form a complex with metal ions. PPI dendrimers are nonporous macromolecules with nanostructures, which are able to

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encapsulate heavy metal pollutants. Considering these advantages, they represent promising new superabsorbents.[15] The present study aimed to investigate the adsorption of cadmium and nickel from aqueous solutions using the PPI dendrimer and assess the influential factors (pH, PPI dosage, and initial concentrations of cadmium and nickel) using a batch model. Furthermore, we evaluated the mechanism of adsorption and calculated the maximum adsorption values using the Langmuir and Freundlich isotherms.

Materials and Methods

PPI dendrimers G2 were purchased from Sigma-Aldrich (USA), and the standard solutions of cadmium and nickel (1 g/L) were prepared using sulfate salts. The other materials and reagents were provided by Merck (Germany) and Sigma-Aldrich companies. The concentrations of the heavy metals were determined using inductively coupled plasma (ICP) (Optima 2000 DV). The functional groups were assessed using the Fourier transform infrared spectroscopy (FTIR) spectra in KBr pellets by a Tensor 27 spectrophotometer (Bruker Optik GmbH, Germany) in the wave numbers of 500-4,000 1/cm. In addition, atomic force microscopy (AFM; ARA Research Co., model: No. 0101/A, Iran) was used to analyze the surface roughness. The pH of the solutions was regulated using HCl and NaOH solutions and measured using a Metrohm pH-meter (model: E 647, Germany), which was supplied with a glass combination electrode.

The adsorption analyses were carried out at the pH of 2-7, metal ion concentrations of 50-200 mg/L, and PPI dosage of 0.04-1 g/L. To assess the mechanism of adsorption and calculate the maximum adsorption values, the Langmuir and Freundlich isotherm models were used.

Results and Discussion

Fig. 1 shows the FTIR spectra of the PPI dendrimer in the region of 500-4,000 1/cm. Accordingly, the PPI dendrimer showed the N-H band at 3,271 and 1,545 1/cm, C-H band at 2,951 1/cm, and C-N band at 1,000-1,350 1/cm. Adsorbent was a key influential factor in the adsorption process, which was significantly lower due to the large specific surface and could adsorb the pollutants with higher capacity.

Dynamic light scattering (DLS) was performed in order to characterize the self-assembled structure of the dendrimer. According to the DLS analysis (Fig. 2), the mean diameter of the PPI dendrimer was 1-10 nm. The shape and surface topology of the PPI dendrimer are depicted in Fig. 3. As can be seen, spherical particles were detectable in regular intervals without the spreading of the molecules. The roughly spherical structure could justify the aggregates of the dendrimers on the surface of the silica. Based on the cross-sectional line scans along the segment, the height of the dendrimers was estimated at 15 nm.

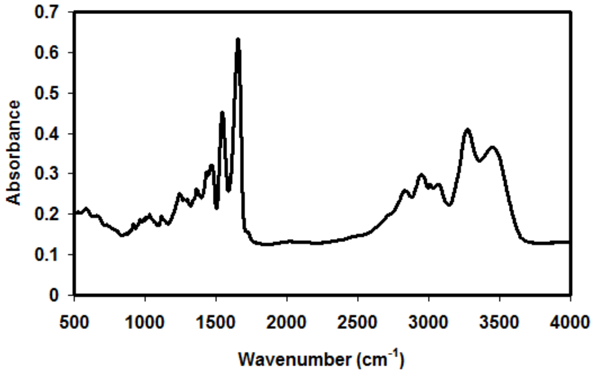

Fig. 1. FTIR spectrum of PPI dendrimer

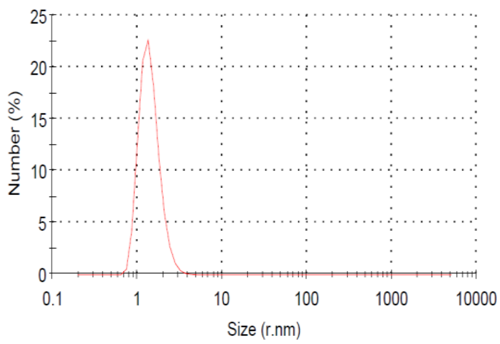

Fig. 2. DLS analysis of PPI dendrimer

Effect of pH

The pH of the liquid phase significantly affected the adsorption of the heavy metal ions from wastewater as it ascertained the surface charge of the sorbent and adsorbate.

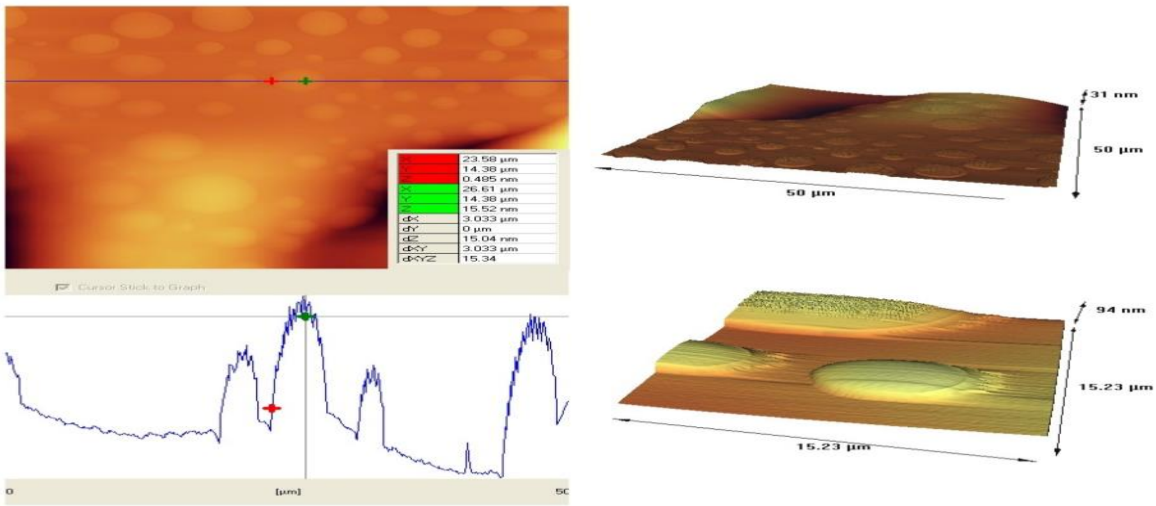

Fig. 3. AFM images of dendrimer

The effect of pH on the uptake of heavy metals with the PPI dendrimer was investigated within the pH range of 2-7 with determined concentrations of the heavy metal ions (100 mg/L). As is depicted in Fig. 4, the uptake rate of cadmium and nickel enhanced from the pH of two to the pH of seven, and the maximum adsorption of both heavy metal ions was observed at the pH of seven. Therefore, pH of seven was selected as the optimal pH for further assessments. The low uptake of these heavy metals at acidic pH was attributed to the electrostatic repulsion between the positively charged PPI surface and heavy metal ions.

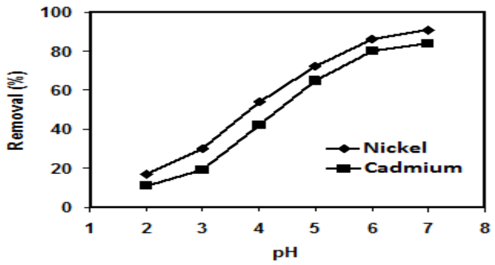

Fig. 4. Effect of pH on cadmium and nickel removal by PPI dendrimer (C_0=100 mg/L, $C_{adsorbent}$=0.08 g/L, T=298 °K)

Nevertheless, when the pH enhanced, the surface charge of the PPI dendrimer became more negative.[16]

Effect of the adsorbent dosage

The adsorbent dosage was considered to be a major parameter since it specified the capability of the adsorbent for the determined initial concentration of the heavy metals. The uptake of cadmium and nickel was assessed based on various dosages of the PPI dendrimer (0.04-0.1 g/L). As is illustrated in Fig. 5, the uptake rate of the heavy metal ions increased with the enhancement of the PPI dosage, which could be attributed to its high accessible adsorption sites. In addition, the maximum uptake of cadmium and nickel was achieved with 0.08 g/L of PPI, which was selected for further analysis.[17]

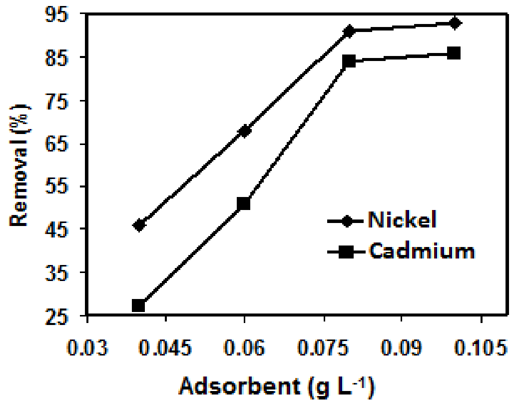

Fig. 5. Effect of adsorbent dosage on heavy metal removal by PPI dendrimer (C_0=100 mg/L, pH=7, T=298 °K)

Effect of the initial heavy metal concentration

The effect of the initial heavy metal concentration was investigated within the range of 50-200 mg/L, and the results are shown in Fig. 6. As can be seen, the adsorption efficiency of cadmium and nickel by the PPI dendrimer enhanced with the increased concentration of the heavy metal ions due to the accessibility of adsorption sites on the PPI. However, as the cadmium and nickel concentrations became extremely high, the removal efficiency decreased.[18]

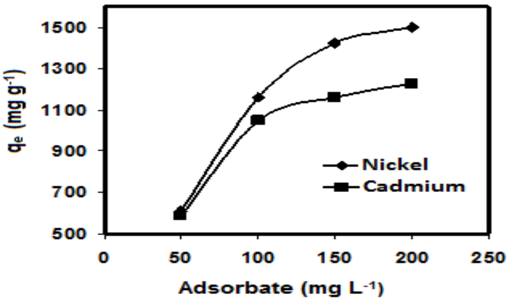

Fig. 6. Effect of initial heavy metal concentration on cadmium and nickel removal by PPI dendrimer (pH=7, $C_{adsorbent}$=0.08 g/L, T=298 °K)

Adsorption isotherms

Adsorption isotherms are used to explain adsorption saturation in wastewater operations. In the current research, the adsorption data were fitted to Langmuir and Freundlich isotherm equations. The Langmuir model is reliable owing to the single-layer adsorption on the surface, and the Freundlich model is used to explain multi-layer adsorptions with bonding among the adsorbed molecules. The linear equations of the Langmuir and Freundlich models are present as Eqs. 1 and 2, as follows:[19]

$$log\, q_e = log\, K_F + \frac{1}{n} log\, C_e \qquad (1)$$

where K_F is the adsorption capacity, *1/n* represents the adsorption intensity, and *1/n* shows the type of the isotherm to be double-faced (1/n=0), desirable (0<1/n<1), and undesirable (1/n>1).

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \qquad (2)$$

In Eq. 2, q_e, C_e, Q_0, and K_L are the values of the adsorbed heavy metals at the equilibrium (mg/g), metal concentration at the equilibrium (mg/L), maximum adsorption capacity (mg/g), and Langmuir constant (l/mg), respectively.

Table 1 shows the obtained results by the coordination of the empirical saturation state data to the isotherm models with the correlation-coefficients (R^2) of the Langmuir and Freundlich models.

Table 1. Isotherm parameters of cadmium and nickel adsorption by PPI dendrimer (pH=7, adsorbent=0.08 g/L, T=298 °K)

	Langmuir Isotherm			Freundlich Isotherm		
	Q_0	K_L	R^2	K_F	N	R^2
Ni	1428	0.041	0.999	396	4.857	0.920
Cd	1250	0.034	0.999	363	5.464	0.919

The evaluation of the linear plots demonstrated that for the adsorption of cadmium and nickel onto the PPI dendrimer, the Langmuir isotherm was fitter and had a higher correlation-coefficient (R^2=0.999) compared to the Freundlich isotherm. Therefore, the adsorption of cadmium and nickel by the PPI dendrimer better conformed to the monolayer system (Fig. 7).

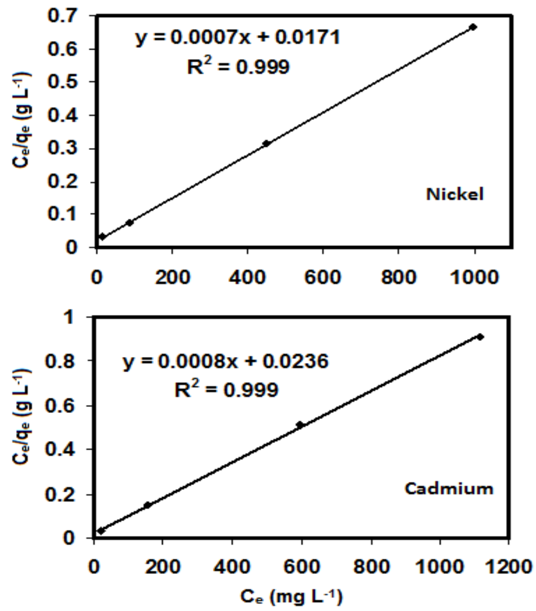

Fig. 7. Liner Langmuir isotherm of cadmium and nickel removal by PPI dendrimer (pH=7, adsorbent=0.08 g/L, T=298 °K)

Conclusion

According to the results, the PPI dendrimer as the navel adsorbent could be applied for the uptake of cadmium and nickel from aqueous solutions. The experiments were carried out using a batch system, and the effects of pH and adsorbent dosage indicated that the increased values of these parameters was associated with the higher rate of heavy metal ion removal. On the other hand, the increased concentration of the heavy metal ions was associated with the reduced rate of heavy metal adsorption.

In order to assess the mechanism of adsorption and calculate the maximum adsorption values, the Langmuir and Freundlich isotherms were used. The results of the DLS analysis indicated that the mean diameter of the PPI dendrimer was 1-10 nm, while the maximum adsorption of both heavy metal ions occurred at the pH of 7. The maximum uptake of cadmium and nickel was achieved at the adsorbent dosage of 0.08 g/L. The Langmuir isotherm model coordinated the saturation state data better than the Freundlich model with a higher correlation-coefficient (R^2=0.999). The maximum removal capacity of PPI was 1,428 and 1,225 mg/g for nickel and cadmium, respectively. Therefore, it was concluded that the type of the dendrimer was a potential adsorbent, which was able to uniquely uptake large quantities of heavy metals in the liquid phase.

Acknowledgments

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