Research Article

Synthesis of Poly(Ortho-Phenylenediamine) Fluffy Microspheres and Application for the Removal of Cr(VI)

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We reported the synthesis of fluffy poly(o-phenylenediamine) (PoPD) microspheres via chemical polymerization of oPD monomers by ammonium persulfate (APS) at room temperature. The SEM images showed that PoPD microspheres with an average diameter of 1.5 µm and their surfaces consist of highly oriented nanofibers. Furthermore, PoPD microspheres were used as adsorbent materials for the removal of Cr(VI) from aqueous solutions. The Cr(VI) adsorption behavior on the prepared PoPD microspheres was studied at different adsorption contact times, solution pH values, and amount of the adsorbent. Experimental isotherms of Cr(VI) ions were successfully fit to the Langmuir isotherm model. The results indicate that the PoPD fluffy microspheres are an effective adsorbent for the removal of Cr(VI) ions from aqueous solutions, and they could be useful in treatment of Cr(VI)-polluted wastewaters.

1. Introduction

Heavy metal ions and their compounds are widely used in different industries such as metallurgy, battery, paper, and paint manufacturing [1]. The excessive use of heavy metal ions is increasing their amounts in aquatic systems. Heavy metal ions are among the most important pollutants in waters. They are nondegradable and therefore continue to accumulate in water bodies [2]. Because of their toxic properties and the tendency for bioaccumulation in the food chain, it is necessary to take effective routes to reduce the concentration levels of heavy metals in waters [3]. Among all heavy metals, Cr(VI) ingestion beyond permissible quantities causes various chronic disorders in human beings. Chromium present in aqueous systems in both the trivalent form Cr(III) and hexavalent form Cr(VI) has been placed on the top of a list of priorities of toxic pollutants by the US Environmental Protection Agency (USEPA). Compared with Cr(III), Cr(VI) with its higher solubility in water contaminated by electroplating, steel manufacturing, dying, and so forth are more harmful to living organisms [4]. Thus, the removal of Cr(VI) ion in contaminated water is of great importance.

The various methods of removal of Cr(VI) from industrial wastewater include filtration, chemical precipitation, adsorption, electrodeposition, and membrane systems or even ion exchange processes. The chemical precipitation and reduction process need other separation techniques for the treatment and disposal of high quantities of waste metal residual sludge produced. These techniques use a lot of treatment chemicals and the residual Cr(VI) concentration required in the treated wastewater is not achieved because of the structure of the precipitates. The application of membrane systems for wastewater treatment has major problems like membrane scaling, fouling, and blocking. The drawback of the ion exchange process is the high cost of the resin, while the electrodeposition method is more energy intensive than other methods. Among these methods, adsorption is one of the most economically favorable and technically and easily feasible method [5].

Due to the increasing consciousness of cost effectiveness and public environmental protection, lower-cost, more efficient, and safer adsorbents for the treatment of industrial wastewaters contaminated with heavy metals are now in demand. To date, several recent investigations have focused
on the use of low-cost adsorbents, such as chitosan [6–8], waste materials [9], activated carbon [10], coal [11], and polymers [12–15]. Since the last decade, adsorption of metal ions by conductive polymers such as polyaniline and polythiophene has been reported [12, 15]. Recently, Polymers based on aniline derivatives have also been extensively investigated. Among them, poly(phenylenediamine) homopolymer is reported to be a highly aromatic polymer containing 2,3-diaminophenazine or quinoxaline repeating units [16] and has been subjected to extensive studies for preparation of lightweight battery electrodes, sensors, electromagnetic shielding devices, and anticorrosion coatings because of its controllable electrical conductivity, environmental stability, good redox reversibility, and low cost [17, 18]. PoPD also has been known to have a remarkable selectivity to certain ions. In addition, it has insolvibility and high thermal stability. Electrochemical polymerization has been proven to be an effective method for preparation of PPD films on substrates [19], and, on the other hand, chemical oxidation polymerization is also a good alternative for preparing PPD micro/nanostructures in solution [20–23]. Would we change “quinorline” to “quinoxaline”.

Herein, we reported an approach to the synthesis of fluffy PoPD microspheres in H2SO4 solution. The morphology of the sample was determined by scanning electron microscopy (SEM). The molecular structure of the synthesized fluffy microspheres is characterized by X-ray energy dispersive (EDS). In view of the health problems caused by Cr(VI), the objective of this study was to assess the uptake of Cr(VI) from aqueous solutions onto fluffy microspheres. The influence of several operating parameters for adsorption of chromium(VI), such as contact time, temperature, pH, and adsorbent dose, were investigated in batch mode.

2. Experimental

2.1. Materials and Methods. All chemicals were purchased from Aladin Ltd. (Shanghai, China) and used as received without further purification. The water used throughout all experiments was purified through a Millipore system. All glassware was cleaned in a bath of freshly prepared aqua regia solution (HCl/HNO3, 3:1) and then rinsed thoroughly with ultra pure water. The stock solution (1000 mg L−1) was prepared by dissolving 2.829 g of potassium dichromate (K2Cr2O7) in 1000 mL of ultra pure water. All working solutions of possessing varying concentrations were obtained by successive dilution. For batch studies, After reaching equilibrium, the sorbent solution was centrifuged and analyzed for the chromium content using an atomic absorption spectrometer (Beijing Rayleigh WFX-120 Model) with 0.078 ppm chromium detection limit.

2.2. Synthesis of PoPD Fluffy Microspheres. In a typical experiment, 0.25 mM oPD aqueous solution was diluted with water to 10 mL, followed by the addition of 2.5 mL of 0.1 M APS aqueous solution under shaking. Then the reaction was allowed to proceed without agitation for 24 h at room temperature. The resulting precipitates were washed with water by centrifugation twice first and dried in a vacuum at room temperature for characterization and further use.

2.3. Sample Characterization. The morphologies of the samples were determined by scanning electron microscopy (SEM) using a JSM-6510LV (Rigaku, Japan) equipped with an Inca X-Max energy dispersive (EDS). Fourier transform infrared (FTIR) was performed on a Nicolet 6700 (resolution 0.4 cm−1) infrared spectrometer and samples were dispersed in potassium bromide and compressed into pellets.

2.4. Effect of Contact Time. The contact time of adsorbent with adsorbate is of great importance in adsorption since contact time depends on the nature of the system used. Adsorption experiments for Cr(VI) on PoPD were carried out as follows: To each of 0.4 g the PoPD sample, 100 mL of solution containing 50 mg L−1 of Cr(VI) was added. The solution was adjusted with 0.1 M HCl and 0.1 M NaOH solutions to pH 4. The samples were shaken at 24°C for periods ranging from 5 min to 1.5 h and then centrifuged and 5 mL portions of liquid phases were measured.

2.5. Effect of pH. The pH of the aqueous solution is a significant controlling factor in adsorption process, in order to optimize the pH for maximum removal efficiency, the effect of pH on the removal of Cr(VI) is investigated by varying the pH values from 2 to 12 at a temperature of 24°C and for fixed initial Cr(VI) concentration of 50 mg L−1. The contact time has been fixed at 1.5 h for all experiments.

2.6. Effect of the Amount of Adsorbent. Under optimum conditions of shaking time and pH 4, the effect of adsorbent dosage on the removal of Cr(VI) at C0 = 50 mg L−1 was also studied by shaking 100 mL of metal solution with 0.10 to 0.60 g of the adsorbent.

2.7. The Adsorption Isotherm. The adsorption isotherm was studied by varying the concentration of Cr(VI) solutions with a fixed dose of adsorbent. To investigate the sorption isotherm, three models, Langmuir, Freundlich, and Temkin isotherm equations, were applied [24–26]. The linear isotherm equations were expressed as the following: Langmuir:

\[
\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b},
\]

Freundlich:

\[
\log q_e + \log K + \frac{1}{n} \log C_e = 0.
\]

Temkin:

\[
q_e = A + B \ln C_e,
\]

where \( q_e \) is the equilibrium liquid phase concentration (mg L−1), \( q_e \) is the amount of sorbent adsorbed per unit weight (mg g−1), and \( Q_e \) and \( b \) are the Langmuir constants related to the adsorption capacity and the rate of adsorption, respectively. \( K \) as well as \( 1/n \) are Freundlich constants. The
values of $K$ and $1/n$, which roughly correspond to the adsorption capacity and the heterogeneity factor represent the deviation from linearity of adsorption, respectively. The values $A$ and $B$ are Temkin isotherm constants. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, $R_L$ [27], also known as the separation factor, given by (4)

$$R_L = \frac{1}{1 + bC_0},$$

where $b$ (L mg$^{-1}$) is the Langmuir constant and $C_0$ (mg L$^{-1}$) is the initial highest concentration of metal ion. The value of $R_L$ lies in the range of 0-1 for a favorable adsorption. While $R_L > 1$ represents an unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L = 0$.

3. Results and Discussion

Figure 1(a) shows the SEM images of the morphology of PoPD fluffy microspheres, prepared in the solution that contained 0.25 mM oPD and 0.1 M H$_2$SO$_4$ with the volume ratio of oPD to APS is 1:1. The products are well-defined microspheres with about 1.5 $\mu$m in diameter. From the magnified image inset of Figure 1(a), it can be found that the surface of the obtained microspheres consists of highly oriented nanofibers, similar to the structure of a sea urchin, which is endowed with the availability of larger surface area and more adsorption sites. The chemical composition of these colloids is determined by energy-dispersed spectrum (EDS) (Figure 1(b)). The peaks of C and N are observed, indicating that the particles are formed from oPD. The observation of the peaks of S and O elements can be attributed to the polymerization of oPD by APS which yields the cationic polymer PoPD due to the proton doping effect, the SO$_4^{2-}$ (the reduced product of APS) as counter ions, however, will diffuse into the PoPD structures for charge compensation [28, 29]. All the above observations indicate the successful formation of PoPD colloids.

The chemical structures of PoPD spheres were characterized by FTIR spectra (Figure 2). The peaks at 3374 and 3193 cm$^{-1}$ correspond to the N–H stretching vibrations of the –NH– and –NH$_2$ groups, respectively. Two peaks center at 1623 and 1528 cm$^{-1}$ are ascribed to the C=C stretching vibrations of quinoid and benzoid rings, while the peaks at 1367 and 1235 cm$^{-1}$ are assigned to the C–N stretching vibrations in the quinoid and benzoid imine units, respectively. Moreover, the characteristic bands of C–H out-of-plane deformation at 843, 755 cm$^{-1}$, and 597 cm$^{-1}$ suggest the 1, 2, 4-trisubstituted benzene rings. From above analysis, the chemical structure of our synthesized PoPD spheres is consistent with previous reports [28, 29].

The adsorption processes as a function of time to determine the point of equilibrium were studied from the adsorption experiments of Cr(VI) ions onto the PoPD fluffy microspheres. All experiments were run twice and a good reproducibility of the procedures was obtained. The results are shown in Figure 3, where it is clear that adsorption of Cr(VI) ions into the PoPD is rather quick and after 1.5 h, the complete adsorption equilibrium between the two phases is obtained. The amount of Cr(VI) ions removed reached a maximum of 99.04%. No further adsorption above the quantity obtained in 1.5 h of contact time was obtained by placing adsorbent samples in contact with Cr(VI) solutions for 1 day of shaking time. This behavior shows that adsorption of Cr(VI) ions occurred in a single step and that the adsorption before 1.5 h can be explained.

The pseudo first-order and pseudo second-order kinetic models were selected to test the adsorption dynamics in this work because of their good applicability in most cases in comparison with the first and second-order models [30]. The first-order rate expression of Lagergren based on solid capacity is generally expressed as follows:

$$\log(q_e - q_t) = \log(q_e) - \left( \frac{k_1}{2.303} \right)t,$$

where $q_e$ and $q_t$ are the amounts of chromium ions adsorbed (mg g$^{-1}$) at equilibrium and at time $t$ (min), respectively, and $k_1$ is the adsorption rate constant of pseudo first-order sorption (min$^{-1}$). In most cases, the first-order equation of Lagergren did not apply well throughout the whole range of
contact times and is generally applicable over the initial 10–30 min of the sorption process. The plotting of log(\(q_e - q_t\)) versus time deviated considerably from the theoretical data after a short period [31].

The pseudo second-order equation is based on the sorption capacity of the solid phase and is expressed as:

\[
\frac{t}{q_t} = \left( \frac{1}{k_2} \right) q_e^2 + \frac{t}{q_e},
\]

where \(k_2\) is the rate constant of second-order sorption (mg g\(^{-1}\)), \(q_e\) the amount of chromium ions adsorbed at equilibrium (mg g\(^{-1}\)), and \(q_t\) the amount of soluted sorbate on the surface of the sorbent at time \(t\) (mg g\(^{-1}\)) [32].

First-order and pseudo second-order kinetic models were tested, and it was found that the results from \(R^2\) were fitted better to the pseudo second-order kinetic model. The values of the pseudo second-order rate constant obtained are shown in Table 1. \(q_{e1}\) are the amounts of Cr(VI) adsorbed (mg g\(^{-1}\)) at equilibrium for the pseudo first-order equation. \(q_{e2}\) are the amounts of Cr(VI) adsorbed (mg g\(^{-1}\)) at equilibrium for the pseudo second-order equation. \(R^2\) is the correlation coefficients.

In adsorption processes, the adsorption of metal ions on the PoPD surfaces can be reduced or increased by the initial pH values of the solutions. It is widely believed that the mechanism for the adsorption of anions involves a surface complexation phenomenon in the adsorption process. Depending on the type of connection of an anion to an active surface site, the surface complexes formed are classified as inner- and outer-sphere complexes. If the number of protonated surface groups is more than that of dissociated groups, the surface is positively charged and become suitable for anion adsorption [33–35].

Experiments were carried out to examine the influence of initial pH on the adsorption of Cr(VI) ions with 50 mg L\(^{-1}\) solutions. The initial pH of chromium solutions was adjusted from 2 to 12 with HCl or NaOH solutions. The pH stability was verified by periodic measurement. The results obtained are shown in Figure 4. Accordingly, when pH is held in the strongly acidic region, preferably below pH 4.0, over 99% removal was attained. In PoPD, Cr(VI) adsorption follows a typical metal anion adsorption behavior, where negligible adsorption occurs at a high pH and a sharp decrease in adsorption is occurred in alkaline media. Therefore, for anionic chemical species, adsorption decreased when pH is increased. So, it would be expected that the maximum adsorption of chromium(VI) ions could occur at lower pH values, since Cr(VI) ions exist as anionic-charged species depending on the pH of solution. Cr is an active metal that exists in several oxidation states, the hexavalent Cr(VI) forms are Cr\(_2\)O\(_7^{2-}\) and CrO\(_4^{2-}\). The two forms are also pH dependent. The predominant form of Cr(VI) below a pH of 6.0 is Cr\(_2\)O\(_7^{2-}\). Increasing the pH will shift the concentration from the Cr\(_2\)O\(_7^{2-}\) form to CrO\(_4^{2-}\) [35]. This could be explained by the following. Because of oxyanion forms such as Cr\(_2\)O\(_7^{2-}\) of Cr(VI) in acidic medium, and the lowering of pH that causes the surface of the PoPD to be protonated to a higher extent, a strong attraction exists between these oxyanions of Cr(VI) and the positively charged amine groups (–NH\(_3^+\)) [36]. In acidic media of pH 2–6, it can be stated that the adsorbent surfaces might be highly protonated and favor
the uptake of Cr(VI). With a further increase in the pH, the degree of protonation of the surface decreases gradually and hence decreased adsorption is observed [34].

On the other hand, the mechanism of Cr(VI) adsorption by the PoPD doped with sulfuric acid seems to be mostly occurred via anion exchange process. When the acid doped PoPD is treated with an aqueous solution of Cr(VI) ions in acidic media, the $\text{SO}_4^{2-}$ (mobile dopant anion) in the polymer is readily exchanged by dichromate, so the Cr(VI) was removed.

$$\text{PoPD–NH}_3^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{PoPD–NH}_3 \cdot \text{Cr}_2\text{O}_7^{2-}$$

$$\text{PoPD}/\text{HSO}_4^- + \text{HCrO}_4^-$$

$$\rightarrow \text{PoPD}/\text{HCrO}_4^- + \text{SO}_4^{2-} \text{ (solution)}.$$

The results from the dependence of Cr(VI) adsorption by variation of different amount of the PoPD in the system were carried out at pH 4.0 and equilibration time of 1.5 h for the adsorption process and they are presented in Figure 5. The 0.10 to 0.60 g adsorbent was used for treatment of 100 mL of Cr(VI) solution with the initial concentration of 50.0 mg L$^{-1}$. The metal ions removed almost remain unchange after adsorbent dosage 0.40 g. Increase in adsorption with increase in adsorbent dosage attributed to the availability of larger surface area and more adsorption sites. At very low adsorbent concentration, the absorbent surface becomes saturated with the metal ions and the residual metal ion concentration in the solution is large. With an increase in adsorbent dosage, the metal ion removal increases until a certain value is reached; afterward, the removal efficiency is maintained constant even if the PoPD is added. So, 0.40 g of adsorbent is enough for the quantitative removal of Cr(VI) ions from 100 mL of wastewater contaminated with this ion with concentration of 50 mg L$^{-1}$.

Isotherms are represented in Figures 6, 7, and 8 the Langmuir, Freundlich, and Temkin models, respectively. Isotherm parameters for the Langmuir, Freundlich, and Temkin models for the PoPD are reported in Table 2. The correlation coefficients ($R^2$) values are higher for Langmuir isotherm than for the Freundlich and Temkin isotherms. This reinforces the fact that Langmuir isotherm is useful to explain the adsorption of Cr(VI) from the solution on the current adsorbent when it follows the monolayer mode, rather than the multilayer mode. A basic assumption of the Langmuir theory is that the sorption takes place at specific homogeneous sites on the adsorbent. When a site is occupied by an adsorbate, no further adsorption can take place at that site. $Q_0$ and $b$ were determined from the slope and intercept of the plot to be 98.23 (mg g$^{-1}$) and 0.11 (L mg$^{-1}$), respectively. This indicates that the good adsorbing capacity of the PoPD is exhibited. The value of $R_L$ in the present investigation has been found $0 < R_L < 1$. Hence, the adsorption process is very favorable and the adsorbent employed exhibited a good potential for the removal of Cr(VI) from aqueous solution [37].

Cr(VI) adsorption onto PoPD fluffy microspheres was confirmed by using EDS analysis. Figure 9 shows the EDS data of PoPD/Cr(VI) that exhibits a characteristic peak of
Table 2: Parameters of the Langmuir, Freundlich, and Temkin isotherm models.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Q₀ (mg g⁻¹)</th>
<th>b (L mg⁻¹)</th>
<th>R²</th>
<th>K</th>
<th>R²</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>297</td>
<td>98.23</td>
<td>0.11</td>
<td>0.996</td>
<td>36.5</td>
<td>3.41</td>
<td>0.991</td>
<td>47.3</td>
<td>12.7</td>
</tr>
</tbody>
</table>

Figure 7: Freundlich adsorption isotherm for Cr(VI) ions adsorption on the PoPD. Freundlich equation: \( \log q_e = \log K + (1/n) \log C_e \).

\[ y = 1.5453 + 0.2929x \]

Figure 8: Temkin isotherm for Cr(VI) ions adsorption on the PoPD. Temkin equation: \( q_e = A + B \ln C_e \).

\[ y = 47.3092 + 12.7263x \]

Cr(VI) in addition to C and O atoms. This indicates that after Cr⁶⁺ ion adsorption on the adsorbent.

4. Conclusions

The PoPD submicrospheres were easily prepared via chemical polymerization of oPD monomers by ammonium persulfate (APS) at room temperature. The Cr(VI) adsorption behavior on the prepared PoPD fluffy microspheres has been studied at different adsorption contact times solution pH values and the amount of adsorbent. Adsorption equilibrium is attained within a short contact time of 1.5 h and the ion exchange of Cr(VI) ions at the surface of PoPD controls the adsorption process. The process adsorption was fitted better to the pseudo second-order kinetic model. The Cr(VI) ions adsorption was favored at slightly initial acid pH values in the equilibrium under acidic conditions (pH ≤ 4). 0.40 g of adsorbent is enough for the quantitative removal of Cr(VI) ions from 100 mL of water contaminated with this ion with concentration of 50 mg L⁻¹. Experimental isotherms of Cr(VI) ions were successfully fit to the Langmuir isotherm model. The results indicate that the PoPD fluffy spheres are an effective adsorbent for the removal of Cr(VI) ions from aqueous solutions, and they could be useful in treatment of Cr(VI)-polluted wastewaters.

References

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