Efficient removal of Cr(VI) from wastewater using magnetically separable poly(m-phenylenediamine) particles

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Abstract. The magnetic polymer adsorbent Fe₃O₄@poly (m-phenylenediamine) (Fe₃O₄@PmPD) was formed at room temperature (25°C) by chemical oxidative polymerization using Fe₃O₄ and m-phenylenediamine (mPD). The effects of the Na₂CO₃ concentration and Fe₃O₄ mass used in the synthesis on the adsorption capacity were studied. The effects of contact time, initial concentration and temperature on adsorption were individually analyzed. The equilibrium data were evaluated by kinetic and thermodynamic models. The highest adsorption capacity of the material was 654.4 mg/g at room temperature and pH=2. Finally, the recyclability of the materials was tested by cycling experiments. The material could be recycled and retained 73.18% of its initial adsorption capacity after 5 cycles. The magnetic polymer material exhibits excellent hexavalent chromium removal capacity and broad application prospects in the treatment of chromium-containing wastewater.

1. Introduction

Due to increased human activities, especially electroplating, leather tanning, manufacturing refractory materials and alloy, wood preservative processes and other industries applications [1,2], the presence of a large amount of chromium in the environment has become one of the most serious environmental pollution problems, seriously threatening the normal growth of animals, plants and human health [3]. To reduce the impact on public health and the possibility of human exposure to high chromium concentrations, strict control the hexavalent chromium content in water is important [4].

Polyaniline polymers have attracted considerable attention in recent years because of their high specific surface area, high environmental stability, good electrical conductivity and special surface functional group structure [5-7], which hold great promise for applications in many fields, especially in environmental pollution removal [8,9]. Compared with polyaniline, the diamine derivative poly(m-phenylenediamine) (PmPD) has more functional groups, such as amino and imino groups, thereby providing better functionality and superior removal of Cr(VI) from wastewater [10]. Yu et al synthesized a PmPD material by oxidative polymerization. The results show that the removal capacity of Cr(VI) by PmPD with the lowest oxidation state can reach 500 mg/g [10]. However, in practical applications, simple polymer materials have limited further applications due to their susceptibility to oxidation, poor mechanical strength, and difficulties in regeneration and recycling [9,11]. At the same time, the removal efficiency is insufficient due to fewer active adsorption sites and lower surface area [12]. The addition of various carriers such as biomass and clay, activated carbon, magnetic composites is therefore necessary to improve the overall performance of the polymer. Wang and Zhang et al first designed and synthesized magnetic PmPD with a core-shell structure for chromium removal and
adsorption. Studies have shown that the combination of magnetic materials and PmPD results in a material with excellent solid-liquid separation ability; however, the harsh synthesis conditions (0 °C) and insufficient adsorption effect limit the wide application of this material [13]. These related studies have shown that polymer modification can effectively improve the Cr(VI) removal ability. However, the current relevant adsorbent materials still have some disadvantages.

Different from previous research, the synthesis method used in the present study can be polymerized at room temperature, rather than at 0 °C. With the addition of a certain amount of Na₂CO₃ during the synthesis, Fe₃O₄@PmPD composites are created by in situ chemical polymerization of mPD and the magnetic material Fe₃O₄ at room temperature. The polymerization endows the surface of magnetic Fe₃O₄ particles with numerous functional groups to enhance the ability to remove Cr(VI) from sewage and the synthesized polymer material exhibits higher Cr(VI) removal capacity than the polymer prepared by the conventional method. In addition, solid-liquid separation can be quickly and easily achieved through magnetic adsorption. This research contributes to the basis of knowledge for improving polymer preparation methods in the future and provides new ideas for better recycling of adsorbent materials.

2. Experiments and methods

2.1. Synthesis of Fe₃O₄@PmPD

Fe₃O₄@PmPD (same as Fe₃O₄@PmPD (1 M, 0.5 g)) was synthesized by an in situ polymerization method. 10 g of ammonium persulfate (APS) was dissolved in 25 mL of distilled water as an oxidizing agent. In addition, the same volume of a 1 M Na₂CO₃ solution was prepared. Next, 5 g of mPD was added to 85 mL of distilled water and vigorously stirred at 25 °C and 500 rpm for 30 min until the solid monomer was completely dissolved and dispersed. Then, 0.5 g of Fe₃O₄ was added to the monomer solution. The APS and Na₂CO₃ solutions were then added to the mixed solution of mPD and Fe₃O₄ at the same rate within 20 min to initiate and adjust the polymerization process. After the concurrent addition of the oxidant and alkaline solutions, the reaction mixture was stirred for 5 h at 25 °C. To remove the oligomers, inorganic salts and other impurities, the precipitated copolymer was filtered and washed with distilled water, ammonia water (1:1, v/v), and absolute ethanol until the filtrate became colorless. Then, the obtained black powder was dried in a vacuum oven at 60 °C for 24 h. As shown in Table 1, the concentrations of Na₂CO₃ and Fe₃O₄ were changed, and polymer materials were prepared with different ratios in the same manner; the obtained products were named as Fe₃O₄@PmPD (0 M, 0.5 g), Fe₃O₄@PmPD (2 M, 0.5 g), Fe₃O₄@PmPD (1 M, 1 g), and Fe₃O₄@PmPD (1 M, 0 g).

| polymer materials | concentrations of Na₂CO₃ | apparent weight proportion of PmPD and Fe₃O₄ |
|-------------------|--------------------------|--------------------------------------------|
| Fe₃O₄@PmPD (1 M, 0.5 g) | 1 M                      | 5 : 0.5                                    |
| Fe₃O₄@PmPD (0 M, 0.5 g) | 0 M                      | 5 : 0.5                                    |
| Fe₃O₄@PmPD (2 M, 0.5 g) | 1 M                      | 5 : 0.5                                    |
| Fe₃O₄@PmPD (1 M, 1 g) | 1 M                      | 5 : 1                                      |
| Fe₃O₄@PmPD (1 M, 0 g) | 1 M                      | 5 : 0                                      |

2.2. Adsorption studies

In a typical experiment, 30 mg of adsorbent was added to a 100 mL Erlenmeyer flask that contained 50 mL of Cr(VI) solution of a given concentration. The pH of the solution was adjusted with 1.5 M NaOH and HCl. At the temperature specified for the experiment, the mixture was stirred at a constant temperature for a certain period at a stirring speed of 500 rpm. Finally, solid-liquid separation was carried out by magnetic separation and syringe membrane filters (0.45 μm). Then, according to the national standard for diphenylcarbazide spectrophotometry, the filtered solution was subjected to UV-vis spectrophotometric analysis to obtain the absorbance, and the Cr(VI) content was evaluated.
The Cr(VI) removal rate was calculated by equation (1):

\[
\text{removal(\%)} = \frac{C_0 - C_e}{C_0} \times 100%
\]

The equilibrium adsorption capacity of the polymer material for Cr(VI) was calculated using equation (2):

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

where \(C_0\) (mg/L) and \(C_e\) (mg/L) are the Cr(VI) concentrations of the initial solution and the solution at adsorption equilibrium, respectively, \(q_e\) (mg/g) is the adsorption capacity at equilibrium, \(V\) (L) is the solution volume, and \(m\) (g) is the amount of adsorbent added.

The regeneration performance of the adsorbent material was subsequently evaluated in a cycling experiment.

3. Results and discussion

3.1. Effect of Fe\(_3\)O\(_4\) and Na\(_2\)CO\(_3\)

![Figure 1](image)

\textbf{Figure 1.} (a) Cr(VI) adsorption capacity of Fe\(_3\)O\(_4\)@PmPD (0 M, 0.5 g), Fe\(_3\)O\(_4\)@PmPD (1 M, 0.5 g), Fe\(_3\)O\(_4\)@PmPD (2 M, 0.5 g), Fe\(_3\)O\(_4\)@PmPD (1 M, 1 g), and Fe\(_3\)O\(_4\)@PmPD (1 M, 0 g). (b) The solid-liquid separation carried out by magnetic separation. (c) The magnetic properties of each type of adsorbent.

To study the effect of different ratios on the Cr(VI) adsorption ability, adsorbents were prepared with different ratios and added to a Cr(VI) solution with a concentration of 300 mg/L. The pH of the solution was adjusted to 2 with NaOH and HCl. The mixture was then stirred at 35°C for 2 h to ensure complete reaction. As shown in figure 1(a), under the same reaction conditions, the adsorption capacity of the adsorbent varied with the concentration of Na\(_2\)CO\(_3\) and Fe\(_3\)O\(_4\). When the mass of Fe\(_3\)O\(_4\) was constant, the adsorption capacity of the material increased with decreasing Na\(_2\)CO\(_3\) concentration. However, when the concentration of Na\(_2\)CO\(_3\) was 0 M, the lowest adsorption capacity among the five
tested materials was obtained; this poor adsorption capacity indicates that the addition of Na$_2$CO$_3$ during the synthesis improves the adsorption performance of the material. However, an excessively high concentration will inhibit this improvement. The conclusions of Yu et al and Zhang et al in previous studies confirm these results [14,15]. Thus, adding suitable additives such as Na$_2$CO$_3$ during the synthesis process and adjusting the pH of the reaction system can affect the oxidation form of the polymerization product, thereby resulting in a material with improved Cr(VI) adsorption ability. When the concentration of Na$_2$CO$_3$ was constant, an excessive amount of Fe$_3$O$_4$ reduced the adsorption capacity of the material. Similarly, Zhu et al found that a Fe$_3$O$_4$–NH$_2$PmPD mass ratio of 1:4 was optimum for hexavalent chromium removal and that the removal capacity was much higher than that of the material prepared with mass ratio of 4:1 [16]; this phenomenon is basically consistent with the results obtained in the present study. Excessive Fe$_3$O$_4$ may reduce the effective functional group content per unit mass of the material, thereby reducing the number of active adsorption sites and the adsorption capacity. Based on the above analysis, Fe$_3$O$_4$@PmPD (1 M, 0.5 g) was determined to exhibit the best adsorption capacity and the optimal ratio.

3.2. Effect of the contact time and initial concentration

Figure 2(a) shows that the adsorption capacity of Fe$_3$O$_4$@PmPD for Cr(VI) increases with time. The capacity rapidly increased during the first 25 min, reaching 95% of the maximum adsorption capacity at adsorption equilibrium. The adsorption capacity slowly increased thereafter. The adsorption equilibrium was achieved after 100 min. The changes in the adsorption capacity may be due to the low pH in the initial stage of adsorption and the high concentration of Cr(VI), which promotes rapid capture and adsorption of Cr(VI) anions by a polymer material with a large number of active sites [17]. In the later stage of adsorption, the active sites on the surface of the material are mostly occupied, and the concentration of Cr(VI) in the solution rapidly decreases with increasing adsorption [18]. The remaining Cr(VI) anions are repelled by the negative charge on the surface of the adsorbent, which is due to the adsorption of anions from the solution. These factors increase the difficulty of material adsorption. Therefore, more time is required to reach adsorption equilibrium than at the initial stage of adsorption. The adsorption of Cr(VI) in solutions with different initial concentrations is also compared in figure 2(b). The solution with an initial concentration of 125 mg/L first reached adsorption equilibrium after 60 min. As the initial concentration increased, the time to reach adsorption equilibrium increased. The time required for the Cr(VI) solution with a concentration of 200 mg/L to reach adsorption equilibrium was the longest. Therefore, the $q_e$ of the material is related to the $C_0$ of the solution. When the initial concentration is higher, the $q_e$ is greater. The reason for this relationship may be that, when the $C_0$ is higher, the amount of residual Cr(VI) anions in solution as the adsorption process proceeds is greater than when the initial concentration is low, and the presence of more anions favors greater adsorption.

**Figure 2.** Effect of (a) contact time and (b) initial concentration on the removal of Cr(VI).
3.3. Adsorption kinetics and adsorption isotherm

Similar to the hexavalent chromium removal behavior of other poly(m-phenylenediamines) [19]. The results of the model fitting shown in figure 3(a) and table 2 indicate that the pseudo-second-order kinetic model has a high correlation coefficient value ($R^2 > 0.98$) and better fits the adsorption behavior of Fe$_3$O$_4$@PmPD in a Cr(VI) solution than the pseudo-first-order kinetic model. In addition, the pseudo-second-order kinetic model gives a $q_e$ simulation value closer to the actual experimental value. Combining the results obtained in these experiments and other existing related research leads to the conclusion that the rate-limiting step of material adsorption is likely chemisorption.

![Figure 3](image)

**Figure 3.** (a) Fits of pseudo-first-order and pseudo second-order kinetic models; (b) fits of the Langmuir and Freundlich isotherm models.

| Table 2. Kinetic parameters for Cr(VI) adsorption by Fe$_3$O$_4$@PmPD. |
|---------------------------------------------------------------|
| Kinetic model       | Initial Cr(VI) concentration |
|                    | 125 mg/L | 150 mg/L | 175 mg/L | 200 mg/L |
| Pseudo first-order equation |
| $R^2$              | 0.950    | 0.913    | 0.918    | 0.914    |
| $q_e$              | 205.576  | 242.231  | 278.697  | 320.686  |
| $k_1$              | 0.259    | 0.298    | 0.312    | 0.325    |
| Pseudo second-order equation |
| $R^2$              | 0.984    | 0.987    | 0.992    | 0.993    |
| $q_e$              | 214.086  | 252.164  | 290.184  | 333.736  |
| $k_2$              | 0.00195  | 0.00188  | 0.00169  | 0.00153  |

Units: $q_e$: mg/g, $k_1$: min$^{-1}$, $k_2$: g/mg/min.

Figure 3(b) shows a fitting analysis of the isotherms of the data obtained by the Langmuir and Freundlich models at different temperatures. Consistent with previous research results, the adsorbent has a higher adsorption capacity at higher temperatures (35°C). To some extent, the adsorption process is an endothermic reaction. Therefore, a high temperature promotes the adsorption reaction. Table 3 shows the parameters related to the Langmuir and Freundlich isotherm. The Langmuir isotherm has a higher correlation coefficient ($R^2$) within the investigated concentration range. This result is similar to the thermodynamic analysis of PmPD materials by Wan et al [19]. The results show that the removal behavior of Cr(VI) by this polymer material is closer to the Langmuir isotherm model. Therefore, the results of the present study show that the adsorption of Fe$_3$O$_4$@PmPD composites is more consistent with the Langmuir isotherm model, indicating that all adsorption sites and energy of the adsorbent are the same and equivalent. In addition, these adsorption sites are uniformly distributed on the surface of the adsorbent and the adsorption on the surface of the material is single-layer adsorption. The adsorbed particles are completely independent and surface contaminants are not transferred.
### Table 3. Adsorption isotherm parameters for Cr(VI) adsorption by Fe₃O₄@PmPD.

| Isotherm model     | Temperature (°C) | 25   | 35   |
|-------------------|------------------|------|------|
| Langmuir isotherm | R²               | 0.906| 0.930|
|                   | q<sub>max</sub>  | 654.387| 754.447|
|                   | K<sub>L</sub>    | 3.842| 2.839|
| Freundlich isotherm| R²              | 0.903| 0.869|
|                   | K<sub>F</sub>    | 387.196| 440.341|
|                   | n                | 8.352| 7.497|

Units: q<sub>max</sub>: mg/g, K<sub>L</sub>: L/mg, K<sub>F</sub>: mg/g.

3.4. Desorption and regeneration studies

After adsorption, the material saturated with Cr(VI) was desorbed with 0.5 M NaOH and the desorbed material was activated with 2 M HCl to regenerate the active sites. The material was separated easily and quickly by solid magnetic separation and regenerated. Figure 4 shows that, after 5 adsorption-desorption cycles, the material still exhibits a good adsorption capacity of 73.18%. This result also shows that during the adsorption process, some irreversible behavior occurs and affects the material regeneration. This phenomenon shows that the magnetic polymer material has excellent cycle regeneration ability and exhibits superior performance compared with traditional adsorbents.

![Figure 4. Effect of the number of adsorption cycles on Cr(VI) adsorption.](image)

4. Conclusions

A magnetic polymer material with an efficient removal ability of Cr(VI) was synthesized by adding a Na₂CO₃ modifier during a conventional polymerization process. When the concentration of Na₂CO₃ was 1M and the dose of Fe₃O₄ was 0.5 g, the resulting material, Fe₃O₄@PmPD (1 M, 0.5 g), exhibited the best performance in removing Cr(VI) from wastewater. Adsorption experiments show that it exhibits much better adsorption performance than conventional PmPD. At the same time, it exhibits good cycle regeneration ability. The solid-liquid separation can be easily and quickly achieved with the application of a magnetic field, thereby making recycling of the material more convenient.

In summary, the prepared magnetic material has strong application potential in the treatment of chromium polluted wastewater. This study provides new ideas and guidance for the further development of Cr(VI) removal materials. However, the environmental effect of regeneration processes is an important consideration for magnetic materials and further research is needed.
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References
[1] Truskewycz A, Shukla R and Ball A S 2018 Phytofabrication of iron nanoparticles for hexavalent chromium remediation Acs Omega 3 10781-90
[2] Kotaś J and Stasicka Z 2000 Chromium occurrence in the environment and methods of its speciation Environ Pollut 107 263-83
[3] Dinker M K and Kulkarni P S 2015 Recent advances in silica-based materials for the removal of hexavalent chromium: A review J Chem Eng Data 60 2521-40
[4] Welling R, Beaumont J J, Petersen S J et al 2015 Chromium Vi and stomach cancer: A meta-analysis of the current epidemiological evidence Occup Environ Med 72 151-9
[5] Meng Y, Zhang L, Chai L et al 2014 Facile and large-scale synthesis of poly(M-Phenylenediamine) nanobelts with high surface area and superior dye adsorption ability Rsc Adv 4 45244-50
[6] Huang M R, Lu H J and Li X G 2007 Efficient multicyclic sorption and desorption of lead ions on facilely prepared poly(M-phenylenediamine) particles with extremely strong chemoresistance J Colloid Interf Sci 313 72-9
[7] Li X-G, Huang M-R, Duan W et al 2002 Novel multifunctional polymers from aromatic diamines by oxidative polymerizations Chem Rev 102 2925-3030
[8] Zare E N, Lakouraj M M and Kasirian N 2018 Development of effective nano-biosorbent based on poly M-phenylenediamine grafted dextrin for removal Of Pb (ii) and methylene blue from water Carbohyd Polym 201 539-48
[9] Yang Z, Ren L, Jin L et al 2018 In-situ functionalization of poly(M-phenylenediamine) nanoparticles on bacterial cellulose for chromium removal Cheml Eng J 344 441-52
[10] Yu W, Zhang L, Wang H et al 2013 Adsorption of Cr(Vi) using synthetic Poly(M-phenylenediamine) J Hazard Mater 260 789-95
[11] Stejskal J 2015 Polymers of phenylenediamines Progress in Polymer Science 41 1-31
[12] Guo X, Fei G T, Su H et al 2011 High-performance and reproducible polyylaniline nanowire/tubes for removal of Cr(Vi) in aqueous solution J Phys Chem C 115 1608-13
[13] Wang T, Zhang L, Li C et al 2015 Synthesis of core-shell magnetic Fe3O4@Poly(M-phenylenediamine) particles for chromium reduction and adsorption Environ Sci Technol 49 5654-62
[14] Yu W-T, Chai L-Y, Zhang L-Y et al 2013 Synthesis of poly (M-phenylenediamine) with improved properties and superior prospect For Cr(Vi) removal T Nonferr Metal Soc 23 3490-8
[15] Zhang L, Chai L, Liu J et al 2011 Ph Manipulation: A facile method for lowering oxidation state and keeping good yield of poly(M-phenylenediamine) and its powerful Ag+ adsorption ability Langmuir 27 13729-38
[16] Zhu H, Wu J, Fang M et al 2017 Synthesis of a core–shell magnetic Fe3O4–Nh2@Pmpd nanocomposite for efficient removal of Cr(Vi) from aqueous media Rsc Adv 7 36231-41
[17] Tang W, Wu Y, Gao T et al 2018 Facile preparation of hybrid porous polyanilines for highly efficient Cr(Vi) removal Rsc Adv 8 33217-27
[18] Wang S, Yang W and Chen G 2015 Graphene-decorated porous ceramics for efficient removal of Cr(Vi) Rsc Adv 5 65982-90
[19] Wan Z, Li M, Zhang Q et al 2018 Concurrent reduction-adsorption of chromium using M-phenylenediamine-modified magnetic chitosan: Kinetics, isotherm, and mechanism Environ Sci Pollut R 25 17830-41