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Heavy Metal Treatment of Municipal Wastewater Based on Chemical Oxidation

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In this paper, based on the existing research, one innovative method for synthesizing poly(m-phenylenediamine) (PmPD) polymer using the chemical oxidation was presented, and the prepared PmPD was used for the treatment of chromium in wastewater. Then, the mechanism of PmPD in the treatment of chromium was studied. The results show that the best method for PmPD synthesis is the drop-by-drop method; 25 °C is the optimum polymerization temperature of PmPD and 5h response time is the optimal synthesis time of the polymer. At pH=2, the removal rate of chromium from wastewater by PmPD polymer reaches more than 80%, and the removal effect of PmPD(Na2CO3)2 on chromium is the best. At pH>7 (the alkaline solution), the PmPD polymer has almost no effect on the removal of chromium. With the same amount of PmPD polymer, the higher the temperature, the better the removal rate of chromium ion by PmPD polymer; the higher the initial chromium ion concentration, the lower the chromium ion removal rate.

1. Introduction

With the rapid development of the global economy, the scale of different industries such as chemical, papermaking, textile, and smelting industry etc. has been constantly expanding. The enterprises above-mentioned will inevitably emit a large amount of toxic chemical industrial wastewater during the production process, causing serious chemical pollution of the water source (Barakat, 2011; Yao et al., 2010). Wastewater contains various types of inorganic waste and non-degradable organic materials. Heavy metal elements are difficult to degrade and are highly toxic. Therefore, it has become the research focus in the field of environmental engineering and municipal areas to treat the heavy metal elements in waste water (Carletti et al., 2008; Dvoretsky et al., 2018).

Chromium is the main heavy metal element in wastewater (Hawley et al., 2010). At present, the methods for treating chromium in wastewater mainly include microbial treatment methods such as precipitation treatment of microorganisms on chromium, microbial adsorption, and microbial reduction etc. (Mohan et al., 2005; Zhang et al., 2013); physical processing method (Mohan, Singh and Singh, 2006; Fahim et al., 2006; Mohan and Jr, 2006; Hirpara, Nikhil and Murty, 2014; Pradhan et al., 2017) such as ion exchange method, separation of thin-film heavy metals, dialysis method (Aşçı and Şefika, 2014; Marzouk et al., 2015); chemical treatment methods mainly including barium salt method, reduction precipitation method, metal oxidation Law etc. (Chang and Kim, 2007; Ma et al., 2013; Mao et al., 2016; Optasanu et al., 2016; Verbinnen et al., 2013).

In this paper, based on the existing methods for treating chromium, the innovative method of PmPD synthesis using the chemical oxidation was proposed, and the prepared PmPD was used for the treatment of chromium in wastewater. Then, the mechanism of PmPD in the treatment of chromium was studied. The research results can provide a new idea for wastewater treatment of municipal engineering.

2. Analysis of PmPD Synthesis and its influencing factors

2.1 PmPD Synthesis based on chemical oxidation

Test materials: m-phenylenediamine, ammonium persulfate, NaOH, $NaCO_3$, ammonia, HCl, acetone, ethanol, NaCl, $NaNO_3$, distilled water, and sodium sulfate etc.

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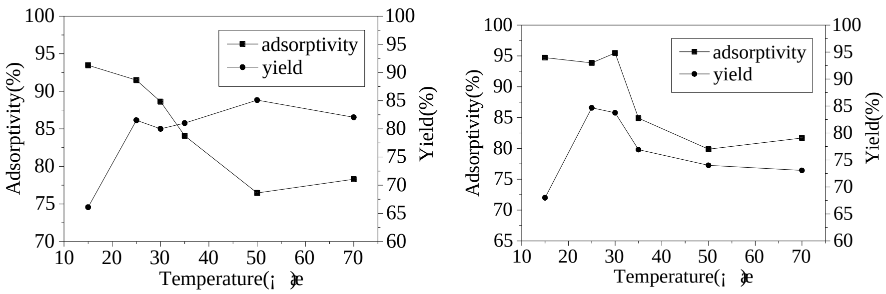
PmPD synthesis based on chemical oxidation is shown as follows:
(1) Accurately weigh 6g of m-phenylenediamine, add it and the distilled water to the flask and mix thoroughly. Then stand still for use;
(2) Prepare certain amount of ammonium persulfate, NaOH, $NaCO_3$ solution for use;
(3) Add both ammonium persulfate and NaOH/$NaCO_3$ solution to the flask at the titration rate of 2ml/min. Always keep stirring during the titration. After the titration, adjust the pH of the solution to 7 and dry to constant weight. In the original solution, the polymerization product produced by titrating the NaOH solution was PmPD(NaOH)x, and that by titrating the $NaCO_3$ solution was PmPD(Na_2CO_3)$_x$. X was the titration concentration.

2.2 Analysis of factors affecting the PmPD synthesis

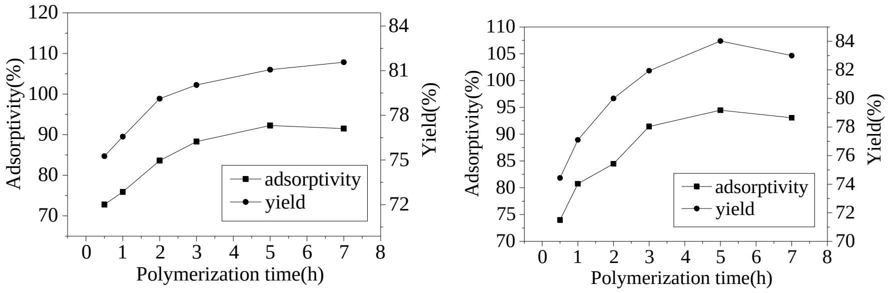
Further analysis was conducted for the factors affecting the PmPD synthesis. Fig.1 shows the effect of different synthesis temperatures on PmPD(NaOH)$_2$/PmPD(Na_2CO_3)$_2$ yield and chromium removal. From Fig. 1(a), it can be seen that the PmPD(NaOH)$_2$ yield gradually increases with temperature, but the chromium removal rate in the wastewater by the resulting polymer product rapidly reduces. The statistical results in Fig. 1(a) indicate that 25°C is the optimum polymerization temperature of PmPD(NaOH)$_2$.



(a) PmPD(NaOH)$_2$ (b) PmPD(Na_2CO_3)$_2$

Figure 1: Effect of different synthesis temperatures on PmPD(NaOH)$_2$/PmPD(Na_2CO_3)$_2$ yield and chromium removal

From Fig. 1(b), with the increase of temperature, the PmPD(Na_2CO_3)$_2$ yield and the removal rate of chromium in waste water show a clear trend of gradual increasing first and then decreasing rapidly, and the statistical results show that 25°C is also the optimal polymerization temperature for PmPD(Na2CO3)2.



(a) PmPD(NaOH)$_2$ (b) PmPD(Na_2CO_3)$_2$

Figure 2: Effect of different synthesis time on PmPD(NaOH)$_2$/PmPD(Na_2CO_3)$_2$ yield and chromium removal

Fig.2 shows the effect of different synthesis time on PmPD(NaOH)$_2$/PmPD(Na_2CO_3)$_2$ yield and chromium removal. From Fig. 2(a) and 2(b), it can be seen that with the reaction synthesis time increasing, the PmPD(NaOH)2/PmPD(Na_2CO_3)$_2$ yield and the removal rate of chromium in waste water show a tendency of increasing gradually; when the reaction time reaches 5h, the yield of the two polymers and the removal rate of chromium reaches the maximum, so the reaction time of 5h is set as the optimal synthesis time.

3. Factors affecting removal of chromium from wastewater by PmPD

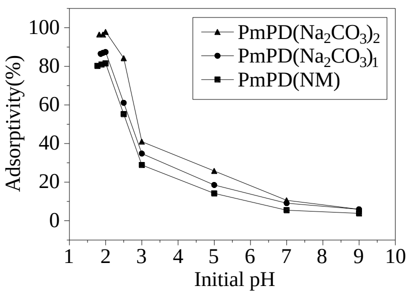


Figure 3: Effect of PmPD on chromium removal at different pH values

Fig.3 shows the effect of PmPD on chromium removal at different pH values. It can be seen from the figure, with the pH of the solution gradually increasing, the removal rate of chromium from three selected PmPD polymers (PmPD($NaOH$)$_2$, PmPD(Na_2CO_3)$_2$, PmPD(NM)) was dropped significantly. When pH exceeds 7 (the alkaline solution), the PmPD polymer has almost no effect on the removal of chromium; at pH=2, the polymer has a chromium removal rate of over 80%, and PmPD (Na_2CO_3) $_2$ has the best removal effect of chromium.

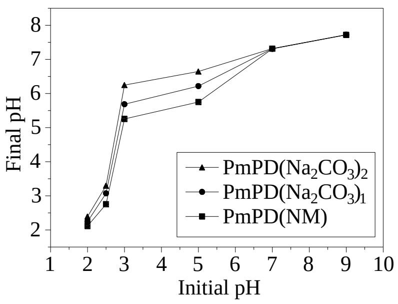


Figure 4: pH change of the solution after removal of chromium from wastewater by PmPD

Fig.4 shows the pH change of the solution after removal of chromium from wastewater by the three polymers (PmPD($NaOH$)$_2$, PmPD(Na_2CO_3)$_2$, PmPD(NM)). It can be seen that, when the chromium in the waste water is removed, the pH of the solution has a certain amount of increase compared to the initial pH. This change can be expressed by formula 1-5.

$$HCrO_4^- \rightarrow H^+ + CrO_4^{2-} \tag{1}$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \text{«} 2Cr^{3+} + 7H_2O \tag{2}$$

$$CrO_4^{2-} + 8H^+ + 3e^- \text{«} Cr^{3+} + 4H_2O \tag{3}$$

$$HCrO_4^- + 7H^+ + 3e^- \text{«} Cr^{3+} + 4H_2O \tag{4}$$

$$H_2CrO_4 + 6H^+ + 3e^- \text{«} Cr^{3+} + 4H_2O \tag{5}$$

From the above formulas, the PmPD polymer can consume the hydrogen ions and protons in the solution during the removal of chromium ions. Fig. 5 shows the change of Cr^{3+} in the solution after removal of chromium by PmPD, indicating that the concentration of Cr^{3+} in the solution gradually approaches zero with the increase of pH value. When the pH is maintained in an acidic state, the content of chromium in the filtrate of PmPD(Na_2CO_3)$_2$ is the largest, and the content of chromium in the filtrates of PmPD(Na_2CO_3)$_1$ and PmPD(NM) is relatively small. This proves again that the polymer PmPD(Na_2CO_3)$_2$ has the best removal of chromium from wastewater.

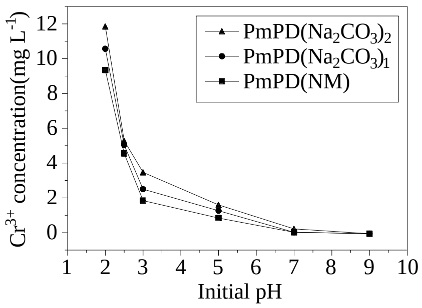


Figure 5: Change of Cr^{3+} in the solution after removal of chromium by PmPD

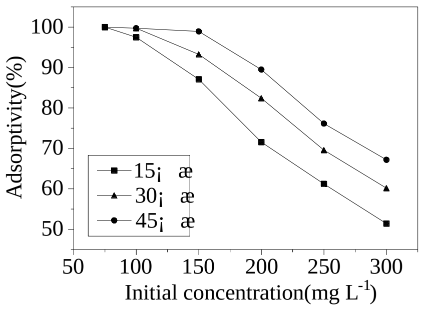


Figure 6: The concentration and removal rate of chromium ion in solution at three temperatures

Fig.6 shows the concentration and removal rate of chromium ion in solution at three temperatures; Fig.7 shows the effect of chromium ion concentration on removal of chromium ion in solution by PmPD at three temperatures. It can be seen from the figures that as the initial chromium ion concentration in the solution gradually increases, in the condition with the same amount of PmPD polymers, the higher the temperature, the higher the removal rate of chromium ion from the PmPD polymer; the higher the initial chromium ion concentration, the lower the chromium ion removal rate.

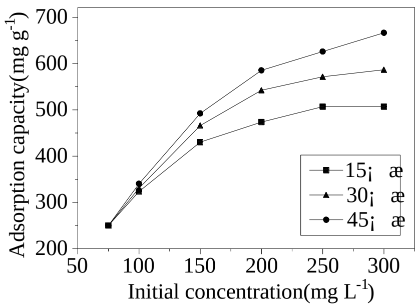


Figure 7: Effect of chromium ion concentration on removal of chromium ion in solution by PmPD at three temperatures

Fig.8 shows the effect of reaction time on the chromium removal by PmPD(Na_2CO_3)$_2$. It can be seen from the figure, as the reaction time increased, the removal effect of PmPD(Na_2CO_3)$_2$ polymer on chromium ions began to show a rapid increase, and at the latter stage, it showed the characteristic of slowly increasing; the higher the temperature, the greater the increase. The reaction tended to balance in about 3 hours. At the initial stage of the reaction, the PmPD(Na_2CO_3)$_2$ polymer mainly makes the filtration of chromium ions through physical adsorption and surface adsorption; in the middle and later stage of the reaction, chromium ions are encapsulated and filtered through permeation.

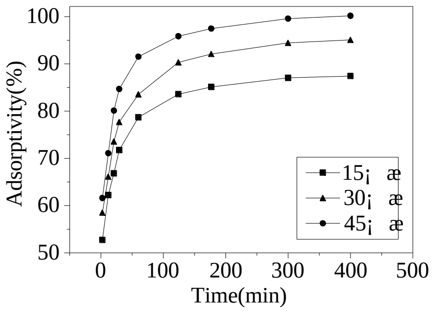


Figure 8: Effect of reaction time on the chromium removal by PmPD(Na_2CO_3)$_2$

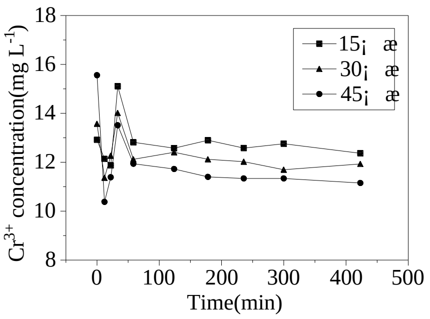


Figure 9: Residual Cr^{3+}concentration in the solution after reaction between PmPD(Na_2CO_3)$_2$ and chromium ions at different reaction temperatures

Fig. 9 shows the residual Cr^{3+}concentration in the solution after reaction between PmPD(Na_2CO_3)$_2$ and chromium ions at different reaction temperatures. It can be seen from the figure, at the initial stage of the reaction, the chromium concentration was strongly oscillating, because PmPD (Na_2CO_3) $_2$ polymer continuously adsorbed Cr^{3+} ions and then reduced the Cr^{3+} ions to metallic chromium. After a certain period of reaction, the variation of chromium concentration was very small, indicating that the adsorption capacity of PmPD(Na_2CO_3)$_2$ polymer for chromium has reached the upper limit.

4. Conclusions

In this paper, based on the existing methods for treating chromium, the innovative method of PmPD synthesis using the chemical oxidation was proposed, and the prepared PmPD was used for the treatment of chromium in wastewater. Then, the mechanism of PmPD in the treatment of chromium was studied. Finally, the main conclusions were made as follows:

(1) The best method for PmPD synthesis is the drop-by-drop method; 25°C is the optimum polymerization temperature of PmPD and 5h response time is the optimal synthesis time of the polymer.

(2) At pH=2, the removal rate of chromium from waste water by PmPD polymer reaches more than 80%, and the removal effect of PmPD(Na_2CO_3)$_2$ on chromium is the best. At pH>7 (the solution is alkaline), the PmPD polymer has almost no effect on the removal of chromium. With the same amount of PmPD polymer, the higher the temperature, the better the removal rate of chromium ion by PmPD polymer; the higher the initial chromium ion concentration, the lower the chromium ion removal rate.

References

Aşçı Y., Şefika K., 2014, Removal of cobalt ions from water by ion-exchange method, Desalination & Water Treatment, 52(1-3), 267-273, DOI: 10.1080/19443994.2013.781544.

Barakat M.A., 2011, New trends in removing heavy metals from industrial wastewater, Arabian Journal of Chemistry, 4(4), 361-377, DOI: 10.1016/j.arabjc.2010.07.019.

Carletti G., Fatone F., Bolzonella D., Cecchi F., Carletti G., 2008, Occurrence and fate of heavy metals in large wastewater treatment plants treating municipal and industrial wastewaters, Water Science & Technology, 57(9), 1329-36, DOI: 10.2166/wst.2008.230.

Chang I.S., Kim B.H., 2007, Effect of sulfate reduction activity on biological treatment of hexavalent chromium [cr(vi)] contaminated electroplating wastewater under sulfate-rich condition, Chemosphere, 68(2), 218-226, DOI: 10.1016/j.chemosphere.2007.01.031.

Dvoretsky D., Dvoretsky S., Temnov M., Markin I., Bushkovskaya A., Golubyatnikov O., Ustinskaya Y., 2018, Technology of using municipal wastewater for obtaining chlorella vulgaris biomass with high lipid content for biofuel production, Chemical Engineering Transactions, 64, 487-492. DOI: 10.3303/CET1864082

Fahim N.F., Barsoum B.N., Eid A.E., Khalil M.S., 2006, Removal of chromium(iii) from tannery wastewater using activated carbon from sugar industrial waste, Journal of Hazardous Materials, 136(2), 303-309, DOI: 10.1016/j.jhazmat.2005.12.014.

Hawley E.L., Deeb R.A., Kavanaugh M.C., Jacobs J.A., 2010, Treatment technologies for chromium(vi), Cheminform, 37(14), 274-303, DOI:10.1002/chin.200614270.

Hirpara P., Nikhil B., Murty D.S., 2014, Bacterial treatment for removal of chromium (vi) containing electroplating waste waters, Indian Journal of Applied Research, 4(6), 436-438., DOI: 10.15373/2249555x/june2014/136.

Ma S., Zhang M., Wang Y., Zhang W., Gong H., Li Q., 2013, Two-stage reduction-precipitation method for the treatment of wastewater containing chromium, Industrial Water Treatment, 33(7), 54-57.

Mao L., Gao B., Deng N., Liu L., Cui H., 2016, Oxidation behavior of cr(iii) during thermal treatment of chromium hydroxide in the presence of alkali and alkaline earth metal chlorides, Chemosphere, 145(3), 1-9, DOI: 10.1016/j.chemosphere.2015.11.053.

Marzouk I., Dammak L., Chaabane L., Hamrouni B., 2015, Optimization of chromium (vi) removal by donnan dialysis, American Journal of Analytical Chemistry, 4(6), 306-313, DOI: 10.4236/ajac.2013.46039.

Mohan D., And K.P.S., Singh V.K., 2005, Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth, Industrial & Engineering Chemistry Research, 44(4), 1027-1042, DOI:10.1021/ie0400898

Mohan D., Jr P.C., 2006, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, Journal of Hazardous Materials, 137(2), 762-811, DOI: 10.1016/j.jhazmat.2006.06.060.

Mohan D., Singh K.P., Singh V.K., 2006, Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth, Journal of Hazardous Materials, 135(1), 280-295, DOI: 10.1016/j.jhazmat.2005.11.075.

Optasanu V., Kanjer A., Montesin T., 2016, High temperature oxidation process affected by shot-peening: Application to pure Zr and Ti, Annales de Chimie: Science des Materiaux, 40(1-2), pp. 69-77, DOI: 10.3166/acsm.40.69-77

Pradhan D., Sukla L.B., Sawyer M., Rahman P.K.S.M., 2017, Recent bioreduction of hexavalent chromium in wastewater treatment: a review, Journal of Industrial & Engineering Chemistry, 55, 1-20, DOI: 10.1016/j.jiec.2017.06.040.

Verbinnen B., Billen P., Van C.M., Vandecasteele C., 2013, Heating temperature dependence of cr(iii) oxidation in the presence of alkali and alkaline earth salts and subsequent cr(vi) leaching behaviour, Environmental Science & Technology, 47(11), 5858-5863, DOI:10.1021/es4001455.

Yao J.L., Wang H.Y., Yu Y.J., Wang Q., Wang X.R., 2010, Pollution status and characteristics of heavy metals in sewage sludge from municipal wastewater treatment plants, Research of Environmental Sciences, 23(6), 696-702.

Zhang H., Zhang X.H., Zhu Y.N., Yuan S.R., 2013, Adsorption of chromium (vi) from aqueous solution by agricultural waste derived activated carbon, Advanced Materials Research, 726-731, 2100-2106, DOI: 10.4028/www.scientific.net/amr.726-731.2100.