International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.5, pp 85-89, 2015

National conference on Nanomaterials for Environmental [NCNER-2015]
19th & 20th of March 2015

Removal of Cr (VI) from tannery effluent using synthesized polyphenylenediamine nanocomposites

Archana S and Jaya Shanthi R*

Department of Chemistry, Auxilium College, Vellore-632006, Tamil Nadu, India.

Abstract : Polyphenylenediamine and their nanocomposites were prepared and characterized using spectral techniques like FT-IR, UV-VIS spectroscopy and the morphology have been studied by XRD, SEM and HRTEM. The stability of the prepared polymer nanocomposites was analyzed using TGA, DTA and found to have high thermal stability. The adsorption of Cr (VI) by synthesized polymer and their nanocomposites was studied and the results showed increased trend of adsorption ability with the incorporation of nanoparticles in the polymer matrix. These conducting polymers and polymer nanocomposites can be effectively made use as adsorbent for the removal of heavy metals, semiconductor devices etc.
Keywords: polyphenylenediamine, nanocomposite, thermal property, adsorption.

Introduction

Chromium is a naturally occurring element found in soil and groundwater in several different forms. It occurs in the (VI) and (III) oxidation states[1]. The major sources of Cr (VI) are from textile dyeing, leather tanning, electroplating, metal finishing industries, oxidative dyeing and water cooling towers which leads[2] to liver damage, pulmonary congestion, oedma and causes skin irritation as well as results in ulcer formation[3, 4].

In general, industrial waste contains both hexavalent and trivalent forms of chromium which are most stable and exist in aqueous system[5]. The hexavalent chromium is of particular concern due to its greater toxicity and it is known to be carcinogenic and mutagenic to living organisms[6]. Different methods have been developed for the removal of heavy metal ions from water and waste water, some of which are precipitation, ion exchange, electrolysis, reverse osmosis, solvent extraction, adsorption and filtration. Among all these techniques, adsorption is the most promising technique and feasible alternatives[7] to remove the heavy metals from the industrial effluents[8].

Many types of adsorbents have been used for the removal of Cr^{6+} and nanostructured adsorbents found to have an excellent ability but it has two defects which seriously restrict their practical applications. The best way is to use the nanoparticles in the form of nanocomposites[9]. A number of nanocomposites have been reported as an efficient sorbents for removal of $Cr^{6+}$from aqueous solution[10].

In the present study, the removal of Cr^{6+} from the textile industry collected from Vellore area was studied using the synthesized polymers and their nanocomposites as an adsorbent.

Materials and Method

The synthesis, characterization of polymers like poly (o-phenylenediamine), poly (p-phenylenediamine)

.
(Abbreviated as PoPDA and PpPDA respectively) and the corresponding polymers with sodium dodecyl sulphate (SDS) and their nanocomposites with 30 weight % of ZnO and TiO_2 nanoparticles was reported in our previous publications[11-13]. The industrial effluent was subjected to ICP analysis and the concentration of chromium present in the solution was above permissible limit. In order to remove chromium from industrial effluent batch sorption methods were adopted.

Adsorption of Cr (VI) from the Industrial Effluent

The adsorption of Cr^{6+} from industrial effluent was studied by spectrophotometer using 1, 5-diphenylcarbazide (DPC) as a complexing agent by dissolving 250mg of DPC in 50mL acetone. The effluent was complexed with diphenylcarbazine solution and measured the absorbance using spectrophotometer at 540nm. The different parameters like effect of pH, the adsorbent concentration and contact time were studied using spectrophotometer. Absorbance of the pink colored solution was measured at λ =540nm after 10min against blank[14, 15]. The percentage removal of Cr^{6+} was calculated using the formula,

$$\text{Removal of } Cr^{6+} (\%) = \frac{Co - Ce}{Co} \times 100$$

Co = Initial Concentration of Cr^{6+} ion.
Ce = Equilibrium Concentration of Cr^{6+} ion.

Results and Discussion

Effect of pH

Experiments were performed at 30°C and initial concentration of 30mg L^{-1} by varying the pH like 1, 2, 3, 4, 5 and 8 as shown in figure 1. It was observed that initial uptake of Cr^{6+} increased with an increase of pH from 1 to 2 thereafter uptake started decreasing with the increase of pH from 2 to 8. The optimum pH for the maximum uptake of Cr^{6+} was found to be 1.0 and this could be explained that, since Cr^{6+} exists in the form of oxyanions such as $HCrO^{4-}$, $Cr_2O_7^{2-}$, CrO_4^{2-} etc., in very acidic medium like 1and this lower pH causes the surface of the adsorbent to be highly protonated and as a result, exists a strong attraction between the oxyanions of Cr^{6+} and positively charged surface of the adsorbent[8]. Hence, the adsorption of Cr^{6+} increases with the decrease in pH. At higher pH like above 4, the adsorbent surface will be negatively charged and in addition, there will be abundance of negatively charged hydroxyl ions in aqueous solution and these two factors can cause hindrance in the adsorption of negatively charge $Cr_2O_7^{2-}$, CrO_4^{2-} etc., resulting in the decrease uptake of Cr^{6+} ion[15, 16].

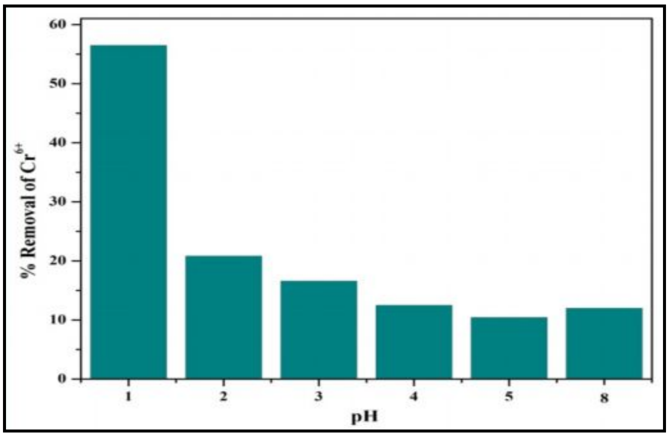

Figure 1. Adsorption of Cr (VI) at Different pH

Effect of Adsorbent Concentration

The effect of adsorbent[17] concentrations like 10, 30, 50, 75 and 100mg was studied for the polymers synthesized with and without the surfactant SDS and the polymer nanocomposites synthesized from 30% of ZnO/TiO_2 nanoparticles. The adsorbents were mixed with effluent solutions and stirred at room temperature for 2h. The adsorption capacities for different doses were determined by keeping pH and contact time constant. The

.
effects of adsorbent dose on the adsorption of Cr^{6+} are given in figure 2. From the analysis it is inferred, that the removal of Cr^{6+} increases with the increase in the adsorbent dose of prepared polymers and their nanocomposites and this may be due to the greater availability of the exchangeable sites and the surface area. As the concentration increases, the available sites and the surface area of the adsorbent increases and this is responsible for the efficient adsorption of Cr^{6+} at higher concentration of the adsorbent. The increase in adsorbent dosage to above 100mg did not have any further adsorption of Cr^{6+} and this suggests that maximum adsorption concentration was fixed as 100mg which was considered for the further studies.

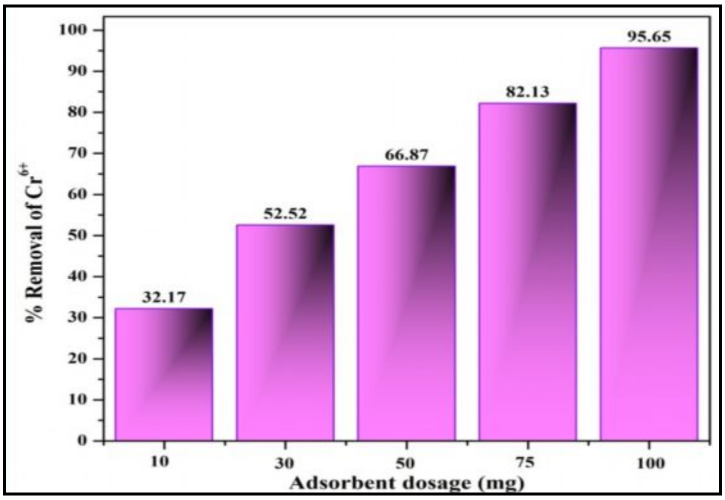

Figure 2. Adsorption of Cr (VI) at Different Adsorbent Dosage

Effect of Contact Time in the Adsorption of Chromium

The contact time has a significant influence on the adsorption of Cr^{6+} and the adsorption studies were carried out at different time intervals, varied from 15 to 150 min and the results are presented in figure 3. The results shows that the adsorption of metal increases with increase in contact time. The adsorption of chromium from tannery effluent increased significantly with increase of the contact time. The metal ions are absorbed by the synthesized polymers and their nanocomposites and the removal efficiency of Cr^{6+} was found to be higher at optimum time of 120 min. Further increase in contact time had negligible effect on the percentage removal of Cr^{6+}. From this study the contact time was fixed as 120 min for the removal of Cr for the further studies.

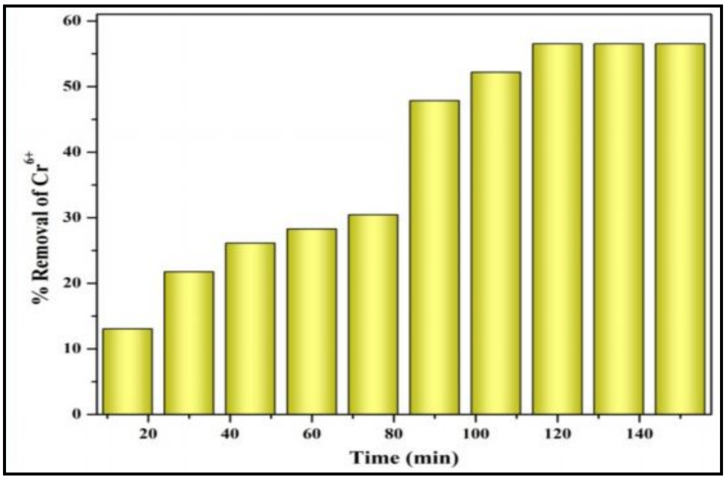

Fig 3 Adsorption of Cr (VI) at Different Time Intervals

The adsorption of Cr^{6+} from the industrial effluent was studied using PoPDA, PoPDA prepared with SDS, polymer nanocomposites synthesized with 30% ZnO/TiO_2 nanoparticles. The pH was maintained to 1 and the polymer and their nanoparticles concentration was fixed as 100mg. In all the experiments, the solution was filtered and measured for Cr^{6+} concentration with the time intervals of 15 minutes. The percentage adsorption of Cr^{6+} with the contact time for the synthesized polymers and their nanocomposites were given in table 1. For the first 15 min the uptake of Cr^{6+} increased rapidly and later, the adsorption becomes slower and reaches saturated state after 120 min. Further increase in contact time made negligible effect on the removal of

.
Cr^{6+}. The fast and rapid uptake of Cr^{6+} in the first 15 min may be due to the fast accumulation of metal ions on the surface of adsorbent and with the further increase of the time, the Cr^{6+} ions further adsorbed in the free sites available in the polymer nanocomposites[18].

Table 1. Comparison of adsorption of Cr (VI) by synthesized polymers and their nanocomposites at different contact time

Time (min)	Removal of Cr (VI) ion (%)							
	PoPDA	PoPDA/SDS	PpPDA	PpPDA/ SDS	PoPDA/ 30% ZnO	PpPDA / 30% ZnO	PoPDA/ 30% TiO_2	PpPDA/ 30% TiO_2
15	43.48	45.22	45.65	47.82	49.56	50	52.17	52.61
30	47.83	52.17	50	52.17	58.7	60.87	58.7	61
45	52.17	54.35	56.52	55.65	60.86	67.39	63.04	65.22
60	56.52	60.86	65.21	67.4	65.22	69.13	69.57	73.04
75	58.69	65.22	69.56	71.74	69.56	71.74	76.09	78.26
90	60.87	67.39	71.74	73.2	74	78.26	78.3	86.96
105	73.92	69.56	73.91	75.65	82.61	83.48	86.96	91.3
120	78.26	73.9	79.13	77.83	85.65	86.96	90	95.65

The maximum adsorption of Cr^{6+} was found for PpPDA prepared with TiO_2 nanoparticles. This is due to the porous structure of polymer nanocomposites as shown in TEM image (Figure 4, 5). The comparison of adsorption ability towards the removal of Cr^{6+} was given in figure 6.

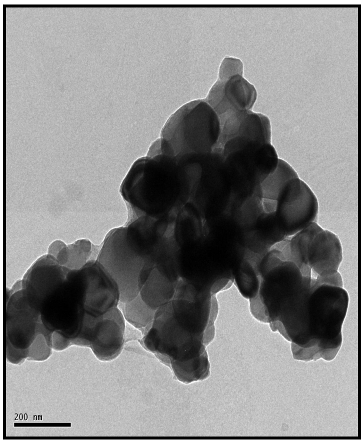

Figure 4. TEM image of PoPDA/TiO_2

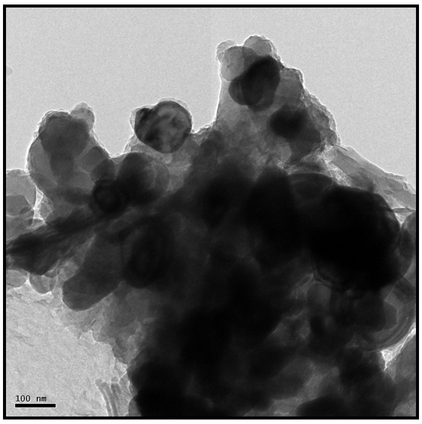

Figure 5. TEM image of PpPDA/TiO_2

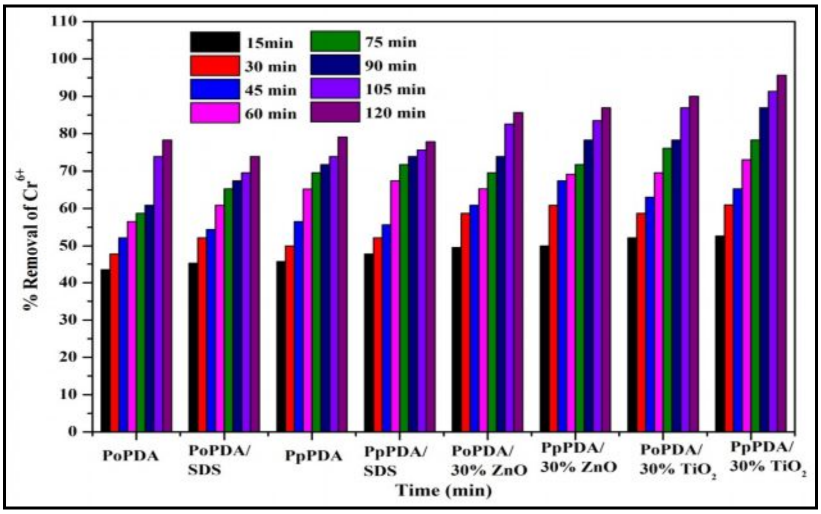

Figure 6. Comparison of Adsorption of Cr (VI) by Polymers and Their nanocomposites as a function of Contact Time

.

Conclusion

Since adsorption is a surface phenomenon, nano adsorbents offer high sorption efficiency and rapid process due to their large surface area and easily accessible sorption sites. Thus the prepared polymer nanocomposites are having higher removal efficiency when compared to their corresponding polymers. The percentage of removal of Cr^{6+} was found to follow the trend:

PpPDA prepared with 30%TiO_2 (95.65%) > PoPDA prepared with 30%TiO_2 (90%) > PpPDA prepared with 30%ZnO (86.96%) > PoPDA prepared with 30%ZnO are (85.65%) > PpPDA (79.13%) > PoPDA (78.26%) > PpPDA prepared with SDS (77.83%) > PoPDA prepared with SDS (73.91%)

References

1. Justyna Jachuła, Zbigniew Hubicki, Applied Water Science, 2013, 3, 653-664.
2. Kotaz J. and Stasicka Z., Environmental Pollution, 2000, 107, 263-283.
3. Raji C. and Anirudhan T. S., Water Research, 1998, 32, 3772.
4. Shajahan Siraj, Md. Monarul Islam, Prokash Chandra Das, Shah Md. Masum, Ismet Ara Jahan, Md. Aminul Ahsan And Md. Shajahan, Journal Of Bangladesh Chemical Society, 2012, 25(1), 53-61.
5. Nakajima A. and Baba Y., Water Research, 2004, 38, 2859-2864.
6. Nakano Y. Takeshita K. Tsutsumi T., Water Research, 2001, 35 (2), 496-500.
7. Das D., Mahapatra R., Pradhan, J., Das S. N., Thakur R. S. Journal of Colloid Interface Science, 2005, 232, 235-240.
8. T. P. Dhungana and P. N. Yadav, Journal of Nepal Chemical Society, 2008/2009, 23, 93-101.
9. Bhaumik M, Setshedi K, Maity A, Onyango M. S., Separation and Purification Technology, 2013, 110, 11-19.
10. N.B.Singh, Sarita Rai and Sonal Agarwal, Nanoscience and technology, 2014, 1-10.
11. Archana S., Jaya Shanthi R., Effect of Surfactant on the Chemical Polymerization of o-Phenylenediamine- A Comparative Study., Indian Journal of Advances in Chemical Science, 2013, 2 (1), 83-88.
12. Archana S., Jaya Shanthi R., Synthesis and Characterization of Poly (p-phenylenediamine) in the Presence of Sodium Dodecyl Sulfate, Research Journal of Chemical Sciences, 2014, 4(2), 60-67.
13. Archana S., Jaya Shanthi R., Dielectric relaxation, AC conductivity and photoluminescence properties of poly (p-phenylenediamine)/TiO2nanocomposites, International Journal of Advanced Research, 2014, 2(10), 778-790.
14. D. Park, Y.S. Yun, J.M. Park, Environmental Science and Technology, 2004, 38, 4860-4864.
15. S.H. Hasan, K.K. Singh, O. Prakash, M. Talat, Y.S. Ho, Journal of Hazardous Materials, 2008, 152, 356-365.
16. ZhoufengWang and Fang Liao, Journal of Nanomaterials, Volume 2012, Article ID 682802, 7 pages.
17. Hemalatha P. V, Prasada Rao P.V. V, International Journal of Environmental Sciences, 2012, 2(4), 2321-2327.
18. KhudbudinMulani, Siona Daniels, Kishor Rajdeo, Sanjeev Tambe, and Nayaku Chavan, Journal of Polymers Volume 2013, Article ID 798368, 11 pages.

*****