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Removal of Chromium from Aqueous Solution using Synthesized Polyaniline in Acetonitrile

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***Abstract*—**Absorptive characteristics of polyaniline synthesized in mixture of water and acetonitrile in 50/50 volume ratio was studied. Synthesized polyaniline in powder shape is used as an adsorbent to remove toxic hexavalent chromium from aqueous solutions. Experiments were conducted in batch mode with different variables such as agitation time, solution pH and initial concentration of hexavalent chromium. Removal mechanism is the combination of surface adsorption and reduction. The equilibrium time for removal of Cr(T) and Cr(VI) was about 2 and 10 minutes respectively. The optimum pH for total chromium removal occurred at pH 7 and maximum hexavalent chromium removal took place under acidic condition at pH 3. Investigating the isothermal characteristics showed that the equilibrium adsorption data fitted both Freundlich's and Langmuir's isotherms. The maximum adsorption of chromium was calculated 36.1 mg/g for polyaniline

***Keywords*—**Polyaniline, Chromium, acetonitrile, Adsorption

I. Introduction

WITH rapid industrial development and population explosion in the world an increasing amount of different pollutants are discharged into environment every day. Some of these pollutants, noticeably heavy metals are potentially hazardous to human health even in minute quantities. Chromium and its compounds are used extensively in some industries such as electroplating, tanning, textile, etc and thus are present in the effluents of these industries. Chromium is most commonly found in two oxidation state namely hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). The hexavalent form is 500 times more toxic than trivalent one [1]. Various methods used for the removal of chromium from aqueous solutions include chemical precipitation, reverse osmosis, ion exchange and adsorption [2]. Among these methods surface adsorption has been considered more effective than others [3] when low concentrations are present. Recently new adsorbents have been studied for chromium removal [4-6] including "Polyaniline" which has shown good potential for absorbing heavy metals from effluents. For example, polyaniline was used for the reduction of toxic hexavalent chromium in water [7].

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Another study was carried out using short chain polyaniline synthesized on jute fiber for removal and recovery of chromium from wastewater [8]. Reduction of hexavalent chromium from water has also been studied using conducting polymer films [9-10].

In this paper, polyaniline was synthesized by oxidation of aniline in mixture of water and acetonitrile in 50/50 volume ratio. Synthesized polyaniline were tested as an adsorbent for removal and reduction of toxic hexavalent chromium from aqueous solutions. Some parameters such as pH of chromium solution, contact time between polymer and solution and adsorption isotherms were investigated.

II. Experimental

A. Materials and Instrumentation

Sulfuric acid, acetonitrile, potassium dichromate, ammonium persulfate and aniline were all provided from "Merck Chemical Company". Chemicals were used without any purification, with the exception of aniline which was distilled under vacuum prior to use.

The magnetic stirrer (MR 3001 K, Heidolph), analysis scale (BP 211 D, Sartorius) and pH meter (CH 9101-Herisau, Metrohm) were applied to experiments. Cr(VI) concentration was measured using UV-Visible Spectrophotometer (Cary 300, Varian) at 375 nm wavelength (maximum intensity seen at this wavelength). Total chromium concentration was measured by Atomic Absorption Spectrophotometer (Spectra AA, Varian) using air–acetylene flame at 429 nm wavelength and slit width of 0.5 nm.

B. Methods

Polyaniline was chemically synthesized by oxidizing aniline monomer under acidic conditions (1M H_2SO_4) in mixture of water and acetonitrile in volume ratio of 50/50 using ammonium persulfate as an initiator of oxidative polymerization. Synthesized polyaniline was grounded and used in powder form.

The hexavalent Chromium solutions were prepared in different concentrations by dissolving potassium dichromate in distilled water. Total chromium (Cr(T), Cr(T)=Cr(VI)+Cr(III)) removal and hexavalent chromium Cr(VI) removal by polyaniline were studied in batch mode. Batch experiments were carried out by contacting 100 mL of hexavalent chromium contaminated solution with predetermined quantities of polyaniline added to it. To achieve the degree of mixing required to reach equilibrium concentration, a magnetic stirrer was employed with speed adjusted at 300 rpm.

Solution pH was ranged from 1–13, fixed by addition of 0.1M NaOH and 0.1N H_2SO_4. After different exposure times chromium solutions were filtered and filtrate was used for measurement of total and hexavalent chromium concentration. The efficiency of total and hexavalent chromium removal has been calculated according to (1):

$$R=100(C_0-C_e)/C_0 \quad (1)$$

Where C_0 is the initial concentration of chromium in solution and C_e is the concentration of chromium after a certain time of exposure with various amounts of polyaniline powder (the equilibrium concentration).

III. Results and Discussion

A. Removal of Cr(VI) from solution using polyaniline

Synthesized polyaniline in a powder shape were used as an adsorbent to remove Cr(VI) from solution. In this experiment 0.1 g sample of polyaniline powder was added to 100 mL of solution containing 50 ppm Cr(VI) at pH 7. The exposure was performed in 30 minutes followed by filtration and separation of polyaniline particles. Results show (Fig. 1) synthesized polyaniline has about three times more removal efficiency than powder activated carbon. When polyaniline was used, total and hexavalent chromium removal rate were not equal. It means that after contact time between polyaniline and Cr(VI) solutions, Cr(III) appears in solutions, which indicates that polyaniline is responsible for reduction of Cr(VI) to Cr(III). Another mechanism is the surface adsorption. It is well known that nitrogen atom in amine derivative makes co-ordinate bond with positive charge of metals due to the presence of electron in s^2p^3 orbit of nitrogen. This co-ordinate bond is the plausible mechanism for adsorption of Cr(VI) and Cr(III) from solution by polyaniline.

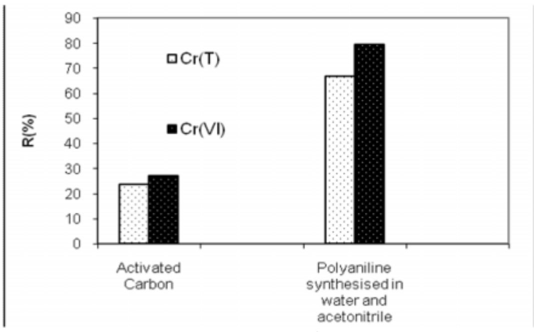

Fig. 1 Removal percentage of Cr(T) and Cr(VI)

B. Effect of agitation time

Equilibrium time is one of the most important parameters in adsorption process. Usually with increase in agitation time removal efficiency increases until equilibrium is reached. In this study fixed amounts of various sorbents (0.1 g polyaniline) were exposed to 100 mL of Cr(VI) solution with concentration of 50 ppm at pH 7 at different equilibration times (2-60 minutes). As results show (Fig. 2) the rate of Cr(T) sorption by polyaniline is high and the removal occurs quickly. For synthesized polyaniline equilibrium time for removal of Cr(T) occurred in 2 minutes.

Although increasing the exposure time generally leads to higher rate of Cr(T) removal, this increase is not significant. According to Figure 3, the optimum time for Cr(VI) removal using synthesized was about 10 minutes.

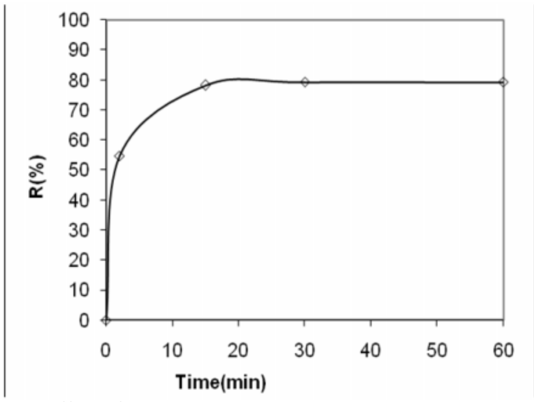

Fig. 2 Effect of agitation time on total chromium removal using synthesized polyaniline

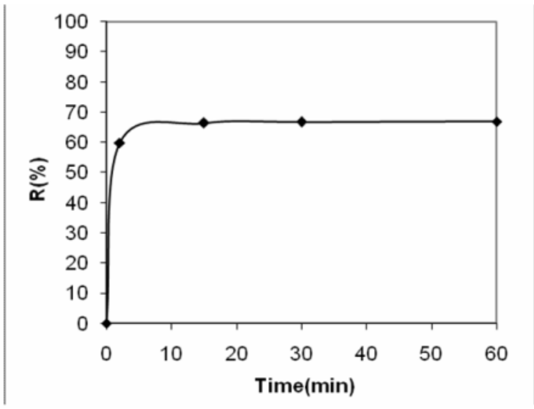

Fig. 3 Effect of agitation time on hexavalent chromium removal using synthesized polyaniline

C. Effect of pH

Solution pH is another important parameter during adsorption process since it reflects the nature of the physicochemical interaction of the species in solution and the adsorptive site of adsorbent. So in this research the effect of pH on adsorption of Cr(T) and Cr(VI) by polyaniline was investigated to find the optimum pH for maximum removal efficiency. In this experiments, 100 mL solution containing 50 ppm Cr(VI) was prepared in different pH values (1–13) using 0.1N H_2SO_4 and 0.1M NaOH solutions. As shown in results (Fig. 4, Fig. 5), high efficiency in Cr(T) and Cr(VI) removal is observed at pH 3-11. Although the maximum Cr(VI) removal occurs at pH 3, the best pH value for Cr(T) removal was found to be 7 for polyaniline. Under acidic conditions, spatially in the highly acidic medium (pH 3) high rate of Cr(VI) adsorption was observed. At acidic pHs the surface of polyaniline is high protonated. The protonated form of polyaniline can form bond with chromate and dichromate anions by electrostatic attraction for high adsorption of Cr(VI) to occur.

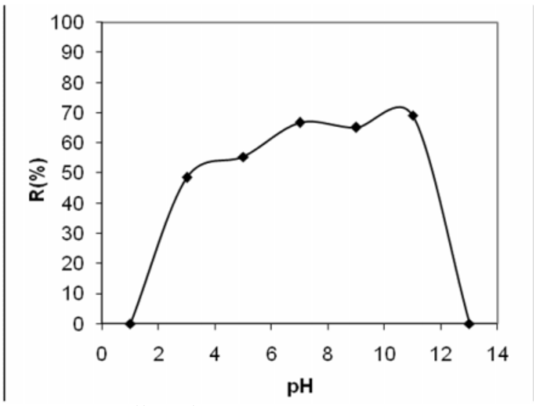

Fig. 4 Effect of pH on total chromium removal

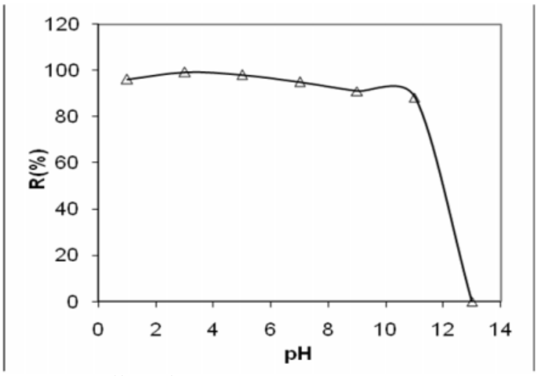

Fig. 5 Effect of pH on hexavalent chromium removal

D. Adsorption isotherms

In order to model the sorption behavior, adsorption isotherms were studied at room temperature. Both Langmuir and Freundlich equations were tested to find the most suitable isotherm model. Langmuir and Fruendlich equations are defined as (2), (3) respectively. The linear form of Fruendlich equation can be shown as (4).

$$1/X = 1/X_m + 1/b\, X_m\, C_e \quad (2)$$

$$x/m = kC_e^{1/n} \quad (3)$$

$$\log (x/m) = \log k + 1/n \log (C_e) \quad (4)$$

Where, C_e is the equilibrium concentration of Cr(T) in solution (mg/l), x is the amount adsorbed (mg), m is a weight of sorbent(g), X is the amount adsorbed by adsorbent (mg/g) and X_m is the maximum amount adsorbed by adsorbent (mg/g). Langmuir isotherm assumes that the number of adsorption sites is fixed and that adsorption is reversible. So, b is Langmuir's constant signifying energy of sorption. The k and n are Fruendlich's constants indicating sorption capacity and intensity, respectively. The plots of 1/X versus C_e and log (x/m) versus log (C_e) enable the constants of Freundlich and Langmuir adsorption isotherms to be determined.

Constant weights of sorbents (0.1 g) were treated with 100 mL of Cr(VI) solution at pH 7 at different initial concentrations (10–50 ppm). Table I shows the concentration of Cr(T) after agitation time between polyaniline and chromium solutions. According to results (Fig.6, Fig.7) adsorption of Cr(T) by polyaniline can be fitted in Langmuir and Freundlich equation.

Table II shows the calculated k, n, b and Xm constants from plots. For a suitable sorbents, constant n in Freundlich equation is normally between 1 and 10. These results indicate that polyaniline can be used as good adsorbents for removal of chromium in solutions. The maximum adsorption of chromium was calculated more than 36.1 (mg/g) for polyaniline.

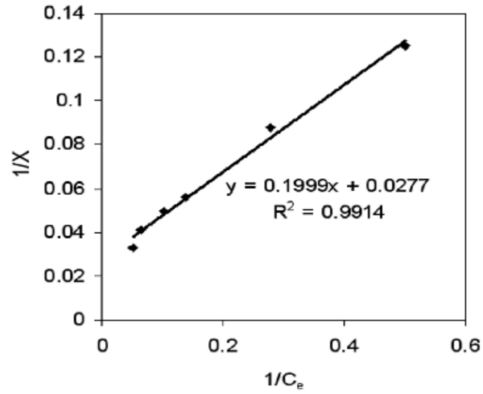

Fig. 6 Adsorption isotherm using Freundlich equation (linear form) obtained for synthesized polyaniline

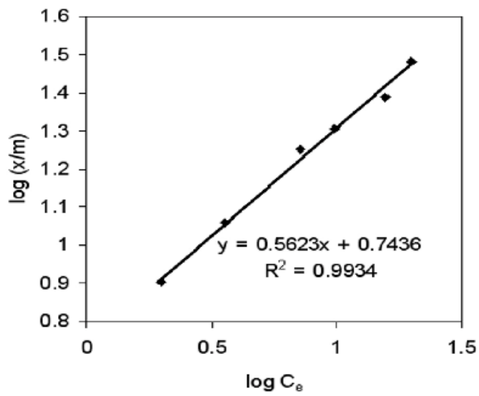

Fig. 7 Adsorption isotherm using Freundlich equation (linear form) obtained for synthesized polyaniline

TABLE I
TOTAL CONCENTRATION OF CR(T) USING POLYANILINE

Initial concentration of Cr (ppm)	10	15	25	30	40	50
Synthesized polyaniline	2	3.6	7.2	9.8	15.6	19.8

TABLE II
COMPARISON OF FREUNDLICH AND LANGMUIR CONSTANT VALUES FOR POLYANILINE

Sorbent	n	k	X_m	b
Synthesized polyaniline in mixture of water and acetonitrile	2	3.6	7.2	9.8

IV. CONCLUSION

In this study synthesized polyaniline in mixture of water and acetonitrile in 50/50 volume ratio was tested as an adsorbent for removal and reduction of toxic hexavalent chromium from aqueous solutions. These results indicate polyaniline can be used as good adsorbent for removal of chromium in solutions with higher efficiencies than activated carbon. The removal mechanism is a combination of Cr(VI) reduction and adsorption of Cr(VI) and Cr(III). The equilibrium time for removal of Cr(T) and Cr(VI) was about 2 and 10 minutes respectively. Maximum Cr(VI) removal occurred at pH=3 and total chromium was removed at neutral pH for polyaniline. The equilibrium adsorption data for all polyaniline fitted both Freundlich's and Langmuir's isotherms. The maximum adsorption of chromium was calculated more than 36.1 (mg/g) for polyaniline.

REFERENCES

[1] Z. Kwalski , "Treatment of chromic tannery wastes", Journal of Hazardous Materials, vol. 37,1994, pp. 137-144.
[2] N. S. Rawat , D. C.Sing, "Removal of chromium in bituminous coal, Asian Environment", vol. 14, 1992, pp. 30-41
[3] K. Selvarj, S. Manonmain, S. Pattabhi, "Removal of hexavalent chromium using distillery sludge", Bioresource Thechnology, vol. 89, 2003, pp.207-211.
[4] M. Liu, H. Zhang, X. Zhang, U. Deng, W. Liu, H. Zhan, "Removal and recovery of chromium from aqueous solutions by a spheroidal cellulose adsorbent", Water Research, vol. 73, 2001, 322-328.
[5] S. Babel , T. A. Kurniawan," Cr(VI) Removal from synthetic waste water using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or Chitosan", Chemosphere, vol. 54, 2004, pp.951-967.
[6] M. Kobya , " Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies", Bioresource Technology, vol. 91, 2004, pp. 317-321.
[7] A. Olad, R. Nabavi, " Application of polyaniline for the reduction of toxic Cr(VI) in water", Journal of Hazardous Materials, vol. 147,2007, pp. 845–851.
[8] P. A. Kumar, S. Chakraborty, M. Ray, " Removal and recovery of chromium from wastewater using short chain polyaniline synthesized on jute fiber", Chemical Engineering Journal, vol. 141,2008, pp. 130–140 .
[9] S. T. Farrell, C. B. Breslin, " Reduction of Cr(VI) at a polyaniline film: influence of film thickness and oxidation state" , Environmental Science Technology, vol. 38, 2004, pp. 4671–4676.
[10] L. A. M. Ruotolo, J. C. Gubulin, "Chromium (VI) reduction using conducting polymer films", Reactive and Functional Polymer,vol. 62, 2005, pp. 141–151.

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