Removal of Chromium from Aqueous Solution Using Two Kinds of Polyaniline

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Introduction

New group of polymers have been synthesized that are electricity conductive. Therefore, they are called conducting polymers. These so-called artificial metals have interesting optical and electrical properties. One of the most conductive polymers is "polyaniline" that is synthesized easily at low cost and with excellent environmental stability. Polyaniline is synthesized chemically and electrochemically in the shape of powder and film. The synthesis condition is noticeably effective on the properties of the produced polyaniline. Reaction temperature, molar ratio of aniline/oxidant, types and concentration of oxidant used in synthesis, will influence the morphology and conductivity of polyaniline. In this paper, Absorptive characteristics of polyaniline synthesized with two different oxidants including potassium iodate and ammonium persulfate has been studied.

Materials and Methods

Sulfuric acid, potassium iodate, and aniline were all provided by "Merck Chemical Company". Chemicals were used without any purification, with the exception of aniline which was distilled under vacuum condition prior to use. In this study polyaniline was chemically synthesized by oxidizing aniline monomer under acidic aqueous conditions (1M H_2SO_4) using ammonium persulfate and potassium iodate as an initiator of oxidative polymerization. Synthesized polyanilines in powder shape is used as an adsorbent to remove toxic hexavalent chromium from aqueous solutions. Experiments were conducted 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 for equilibrium concentration, a magnetic stirrer was employed with a speed adjusted at 300 rpm. Solution pH was ranged from 1–11, fixed by addition of 0.1M NaOH and 0.1N H_2SO_4. After different exposure times, chromium solutions were filtered and filtrates were used for measurement of total and hexavalent chromium concentration.

The efficiency of total and hexavalent chromium removal has been calculated according to the Equation (1):

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

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).

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Discussion of Results

Results show that polyaniline has a removal efficiency of about three times more than powder activated carbon. When polyaniline was used, total and hexavalent chromium removal rates were not equal. It means that after having a 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 the nitrogen atom in polyaniline makes co-ordinate bond with positive charge of metals due to the presence of electron in sp^3 orbit of nitrogen. This co-ordinate bond is the plausible mechanism for adsorption of Cr(VI) and Cr(III) from solution by polyaniline molecules. Synthesized polyaniline with potassium iodate and ammonium persulfate have different Cr(III) and Cr(VI) removal efficiency. The types of oxidant can affect the capacity of polyaniline molecules for removal of chromium. SEM micrographs of synthesized polyaniline with potassium iodate and ammonium persulfate show that the type of oxidant affects surface morphology of synthesized polyaniline (Figures 1, 2). This variation of polyaniline surfaces affects the capacity of prepared polyaniline for chromium removal due to changes of interface between polyaniline and chromium solution.

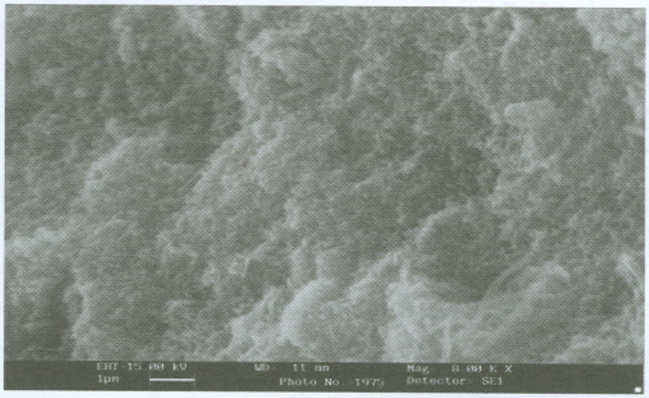

Fig. 1: SEM micrograph (×8000) of synthesized polyaniline with potassium iodate

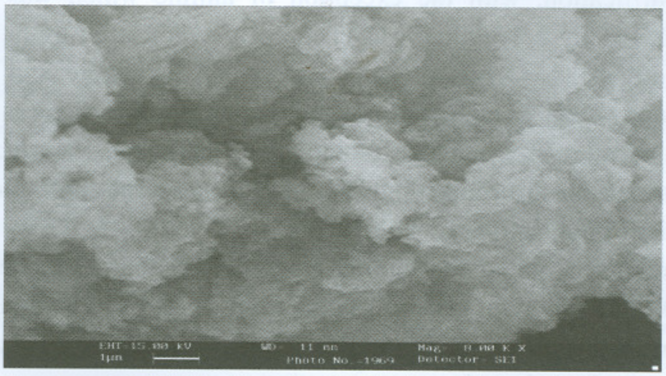

Fig. 2: SEM micrograph (×8000) of synthesized polyaniline with ammonium persulfate

The equilibrium times for total and hexavalent chromium removal were respectively within 30 and 5 minutes for two kinds of polyaniline. 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(III) and Cr(VI) by polyaniline was investigated to find the optimum pH for maximum removal efficiency.

The optimum pH for total chromium removal was 3, 11 for synthesized polyaniline with potassium iodate and ammonium persulfate respectively. Under acidic conditions, especially in a highly acidic environment (pH 1) 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. It is worthwhile to mention that, the oxidizing power of Cr (VI) component increases with decreasing pH. Therefore, reduction process improves under acidic pH using polyaniline.

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 respectively defined as Equation 2 and 3. The linear form of Fruendlich equation can be shown as Equation (4).

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

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

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

Investigating the isothermal characteristics showed that the equilibrium adsorption data for polyaniline fitted both Freundlich's and Langmuir's isotherms. Table 1 shows the calculated k, n, b and X_m constants. For a suitable sorbents, constant n in Freundlich equation is normally between 1 and 10. These results indicate that two kinds of polyaniline can be used as good adsorbents for removal of chromium in solutions. The maximum adsorption of total chromium was calculated 24.44 mg/g and 20.83 mg/g for synthesized polyaniline with potassium iodate and ammonium per sulfate respectively.

During desorption experiments for two kinds of polyaniline about 30% and 65 % of total chromium were released in the solution by using 0.2M NaOH and 0.1M HNO_3 respectively.

Table 1: Comparison of Freundlich and Langmuir constant values for polyaniline

Sorbent	n	k	b	X_m
polyaniline Synthesized with potassium iodate	1.43	0.22	0.07	24.44
polyaniline Synthesized with ammonium persulfate	2	0.92	0.19	20.83

Conclusions

The type of oxidant used in preparation of polymer has a noticeable effect on the capacity of chemically synthesized polyaniline in powder shape for removal of hexavalent chromium from aqueous solutions. Removal mechanism involving polyaniline is the combination of surface adsorption and reduction reaction. Synthesized polyaniline made using potassium iodate had a good performance for total chromium removal, while synthesized polyaniline with ammonium persulfate had the good performance for hexavalent chromium removal. Finally it must also be reflected that synthesized polyaniline can play a major role in removing chromium ions from industrial effluents, with higher efficiencies than activated carbon.

Key words

Polyaniline, Environmental Pollution, Chromium, Adsorption, Reduction.