Removal of Chromium from Waste Water Using Polyaniline

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ABSTRACT: One of the suitable methods for removing heavy metals from waste water is using surface adsorption process. In this article, the preparation of polyaniline and its composites as adsorbents are discussed and the capability of separating chromium from industrial waste water is studied. The results were compared with anthracite and cation exchangers such as purolite-302 and amberjet. The observations indicated that the purolite and amberjet have the most chromium removal percentage. Also the role of polyaniline and its composite as adsorbents were studied. The results show that the percentage of chromium removal has increased in polyaniline/poly(vinyl alcohol) composite. Furthermore, the adsorption percentage is related to the surface morphology, type of adsorbents, and their weight ratios. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1964–1967, 2007

Key words: polyaniline; composites; cation exchangers; chromium removal; surface morphology

INTRODUCTION

Rapid growth in industry and population has resulted in environmental degradation. Heavy metals such as mercury, lead, cadmium, copper, chromium, and nickel are toxic even in extremely minute quantities. Chromium is widely used in chromium-plating, leather tanning, metal finishing, and chromate preparation.

Chromium exists in two stable oxidation states Cr(III) and Cr(VI). The Cr(VI) state is of particular concern because of its toxicity. The recommended limit of chromium in potable water is 0.05 mg/L. The chromium ion (Cr^{3+}) can significantly affect the ecological environment when present in large amounts. Therefore, chromium pollution has recently received much attention in industries.[1]

In recent years, considerable attention has been devoted to fine new adsorbents. Fly ash from a thermal power plant,[2] waste slurry from a fertilizer plant,[3] blast furnace industries,[4] and photo film waste sludge[5] have been examined for removal of hexavalent chromium.

Heavy metals removal from industrial waste streams by the use of natural zeolites has long been applied in medium and large scale installations with variable success.[6] Ion exchange as a conservative technology allows for the simultaneous removal of the metal species and at the same time recovery of pollutants to production lines of origin.[7] Activated carbon with low polar properties is a typical adsorbent and is commonly used for removal of nonpolar organic material in water and waste water.[8]

Polyaniline (PAn) has a reactive NH group in a polymer chain flanked on either side by a phenylene ring, imparting a very high chemical flexibility. It undergoes protonation and deprotonation in addition to adsorption through nitrogen, which, having alone pair of electrons, is responsible for the technologically interesting chemistry and physics. Protonation of PAn not only involves the ingress of protons, but is also accompanied by ingress of anions, to maintain charge neutrality. This suggests that the behavior of PAn depends on the PH and on the counterion of the Bronsted acid used for doping.

Polypyrrole (PPy) is a conjugated polymer with alternating single and double bonds. The conductivity of PPy originates from the π electrons delocalized over the conjugated system and from the doping ions. These ions are interstitially positioned between the polymer chains and may considerably increase the conduction of the polymer. PPy is attractive as an electrically conducting polymer because of its relative synthesis. To exploit this material in some potential commercial applications, it will be necessary to synthesize it at low cost. Bulk quantities of PPy can be obtained as fine powders using the oxidative polymerization of the monomer by selected transition metal ions in water or various other solvents.

Among conductive polymers, PAn has attracted particular interest due to the fact that its electrical properties can be reversibly controlled by changing the oxidation state of the main chain and by protona-

TABLE I
Preparation of Polyaniline Composites

Poly(vinyl alcohol) composite		Quartz composite	
Poly(vinyl alcohol)	1.5 g/L	Quartz	50 g/L
Aniline	0.107 mol/L	Aniline	0.107 mol/L
KIO_3	6 g/L	KIO_3	6 g/L
Reaction time	2 h	Reaction time	2 h
Temperature	Room temperature	Temperature	Room temperature

tion of the imine nitrogen atoms. By coupling the changes in the intrinsic oxidation state of electroactive polymers such as PAn and PPy and their protonation and reduction in acid solution with the decrease in the oxidation state of the metal, electroless precipitation of gold in elemental form from acid solution can be achieved.[9]

The electrophoresis data for PAn-SiO_2, PPy-SiO_2, and PPy-SnO_2 nanocomposites indicate that the surface of these particles are rich in the inorganic oxide component and it is clear that will affect the surface charge of composite particles.[10] The separation of cation may be dependent on reduction/oxidation of PPy or metal/ligand interactions.[11] The addition of a small amount of appropriate polymeric additive such as PVA to conductive polymers can change the structure and the permeability of the film.[12]

The present study was conducted to determine the ability of PAn and its composites to remove chromium from industrial waste water.

EXPERIMENTAL

Instrumentation

Magnetic mixer MK20, digital scale FR200, atomic absorption device perkin-elmer model 2380, pH meter, and scanning electron microscope (SEM) model LSM50A were employed.

Reagents and standard solutions

The experiments have been done at the chromium-plating industry wastewater with the primary chromium concentration of 28 ppm and pH = 2.4. All the materials have high purity degree and have been used without further purification. Distilled deionized water was used throughout this work. Aniline monomer has

been distilled before using. Iodate potassium (KIO_3), anthracite, poly(vinyl alcohol) (PVA, $M_w = 72,000$), sulfuric acid, aniline, Purolite 302, and amberjet cation resins were obtained from Merck (Schuchardt, Germany), Purolite (UK), and Amberjet Company (Lauterbourg, France), respectively.

Polyaniline preparation

For preparation of polyaniline (PAn), 0.6 g KIO_3 was added to 100 mL of sulfuric acid (1M) and then uniform solution was resulted by using magnetic mixer. Then, 1 mL fresh distilled aniline monomer was added to stirred aqueous solution. The reaction was carried out for 2 h at room temperature. Consequently, the resulted polymer was filtered on filter paper and to separate the oligomers and impurities, product was washed several times with deionized water and dried at room temperature.

Polyaniline composites preparation

The reaction was carried out in an aqueous media at room temperature for 2 h. The optimal conditions for composite formation are summarized in Table I.

In a typical experiment, 1 mL of aniline was added to a stirred aqueous solution of 100 mL of sulfuric acid (1M) containing 0.6 g KIO_3 and 5 g quartz or 0.15 g PVA, respectively.

After 2 h, polymer was filtered on filter paper and to separate the oligomers and impurities, product was washed several times with deionized water and dried in at room temperature.

It should be mentioned that in the preparation of PAn composites when the amount of surface active agents such as PVA are low, the stabilization is inefficient and so the macroscopic precipitation of polymer occurs.

TABLE II
The Effect of Different Adsorbents in Chromium Removal

Adsorbent	Cation exchanger Purolite 302	Cation exchanger Amberjet	Anthracite
Initial concentration (ppm)	28	28	28
Final concentration (ppm)	4	5.7	23
Removal percentage (%)	85.7	79.6	17.9

TABLE III
The Effect of Different Surface Adsorbents in Different Weight Ratios in Chromium Removal

Adsorbent	Anthracite/ Purolite mixing in the weight ratio 1 : 1	Anthracite/ Purolite mixing in the weight ratio 1 : 3	Anthracite/ Amberjet mixing in the weight ratio 1 : 1	Anthracite/ Amberjet mixing in the weight ratio 1 : 3	Purolite/ Amberjet mixing in the weight ratio 1 : 1	Purolite/ Amberjet mixing in the weight ratio 1 : 3
Initial concentration (ppm)	28	28	28	28	28	28
Final concentration (ppm)	10	9	9	10.5	4.3	5.4
Removal percentage (%)	64.3	67.9	67.9	62.5	84.6	80.7

Chromium removal method

Completely mixed batch reactor (CMBR) technique was used to remove chromium from industrial wastewater. Hundred milliliters of wastewater was added to the beaker containing 0.5 g of one of the adsorbents and mixed for 30 min by magnetic mixer with its rotating speed of 300 rpm. Then the adsorbent was separated from the solution using filter. The chromium concentration was analyzed by atomic absorption method. It should be noted that the reaction conditions such as temperature, contact time, adsorbent amount, and pH were the same for the experiments carried out in this investigation.

In addition, for calibrating the atomic absorption device, five standard samples with concentration of 5, 10, 30, 60, and 100 ppm were prepared and the corresponding amount of absorption for each concentration were measured. Then by considering the amount of absorption equivalent to each concentration the linear regression curve was drawn. After drawing the calibrating diagram, the samples were injected to the device and their absorption was calculated. Then by considering this diagram the chromium absorption for different solutions were determined.

RESULTS AND DISCUSSIONS

Adsorption is attributed to the affinity interaction between the adsorbent's activated sites and the adsorbate. The adsorption capacity is affected by the adsorbent's properties such as its structure, size, and chemistry of the surface.[13]

The effects of different adsorbents in chromium removal are demonstrated in Table II. As it can be seen, the maximum and minimum adsorption percentage are obtained for purolite 302 and anthracite with 85.7 and 17.9%, respectively.

According to Table III, by mixing the cation exchangers of purolite and amberjet with anthracite in different weight ratios, the removal percentage decreases about 10–20%. Hence, due to the low price of anthracite in comparison to other adsorbents, this method seems to be cost effective.

It has been clearly shown that surface active agents are usually employed to affect the morphology of conducting polymers during chemical polymerization. The total surface area increases as the particle size decreases.

As known PVA is a stabilizing agent and could affect the size, morphology, and homogeneity of particles,[14,15] because the additives are absorbed physically or chemically by the growing polymer.

The effects of PAn and its composites for the removal of chromium from waste water are shown in Table IV. The results show that PAn and PAn/PVA composite have desired procedure in chromium removal with 59.6 and 73.9%, respectively.

Although the chromium removal percentage is decreased to 29.6% by using PAn/quartz composite, but due to the less consumption of polymers in unit weight, it has economical explanation.

The effect of mixtures with different weight ratios are shown in Table V. The results indicated that the purolite 302 and PAn with the weight ratio of 1 : 3 has the most chromium removal (78.6%) and in contrast, the anthracite/PAn mixture has the lowest percentage (21.4%).

The role of PVA on the surface of the PAn particles has to be studied so as to clarify its influence on the structural arrangement of the particles. In Figures 1 and 2, SEM micrographs of the PAn and its compo-

TABLE IV
The Effect of Polyaniline and Its Composites

Adsorbent	Polyaniline	Polyaniline/poly(vinyl alcohol) composite	Polyaniline/quartz composite
Initial concentration (ppm)	28	28	28
Final concentration (ppm)	11.3	7.3	19.7
Removal percentage (%)	59.6	73.9	29.6

TABLE V
**The Effect of Various Adsorbents and Polyaniline in Different Weight Ratios**

Adsorbent	Anthracite/ polyaniline mixing in the weight ratio 1 : 1	Anthracite/ polyaniline mixing in the weight ratio 1 : 3	Purolite302/ polyaniline mixing in the weight ratio 1 : 1	Purolite302/ polyaniline mixing in the weight ratio 1 : 3	Amberjet/ polyaniline mixing in the weight ratio 1 : 1	Amberjet/ polyaniline mixing in the weight ratio 1 : 3
Initial concentration (ppm)	28	28	28	28	28	28
Final concentration (ppm)	15	22	7	6.5	8	6
Removal percentage (%)	46.4	21.4	76.8	78.6	71.4	78.6

sites are shown. As it can be seen the PVA plays a major role on the surface morphology of resultant polymers, because the needle shape of PAn particles, which are obtained in the absence of PVA, are transformed to clusters in the presence of this additive.

CONCLUSIONS

In this study, the effect of PAn and its composites on the removal of chromium from waste water is investigated and the results were compared with various adsorbents such as anthracite, purolite-302, and amberjet. The observations show that the percentage of chromium removal has increased in PAn/PVA composite. Furthermore, in case of PAn/anthracite composite, the adsorption percentage has decreased in comparison to PAn, which has a lower adsorption percentage than purolite and amberjet.

Also, the results show that surface morphology, type of adsorbents, and their weight ratios can affect the amount of adsorption. As it can be seen in the SEM micrographs, PVA play a major role on the surface morphology because the total surface area increases as the particle size decreases.
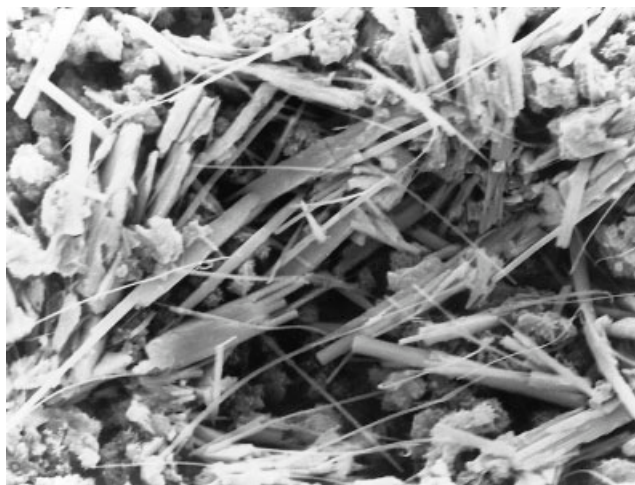
Figure 1 Scanning electron micrograph of PAn (Magnification = 4000×) in an aqueous media without additive. Reaction conditions: KIO_3 = 6 g/L, PAn monomer = 10.7 × 10^{-2} mol/L, volume of solution = 100 mL, reaction time = 2 h at room temperature.
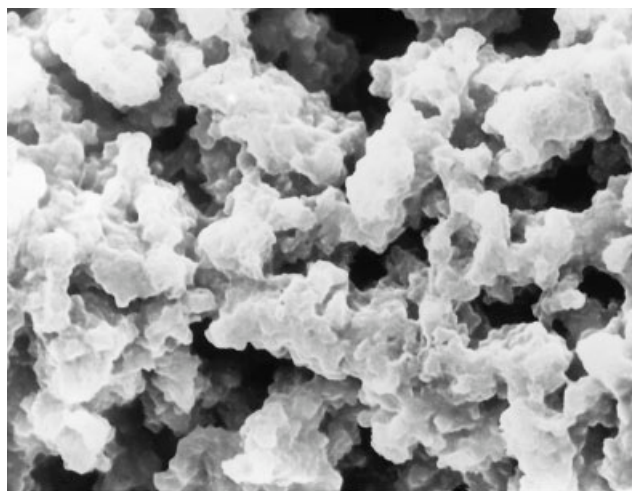
Figure 2 Scanning electron micrograph of PAn (Magnification = 4000×) in an aqueous media using PVA (M_w = 72,000, 1.5 g/L). Reaction conditions: KIO_3 = 6 g/L, PAn monomer = 10.7 × 10^{-2} mol/L, volume of solution = 100 mL, reaction time = 2 h at room temperature.

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