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Redox polymer as an adsorbent for the removal of chromium (VI) and lead (II) from the tannery effluents

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ABSTRACT

Polymer-based hybrid was widely fabricated and applied in heavy metal removal and other inorganic pollutants. The present study deals with the sorption efficiency of metal adsorption through the chemically modified PAA with dihydroxybenzenes into the polymeric matrix present in the tannery effluents and a parallel investigation of chromium (VI) ions in aqueous solution was carried out. From the Langmuir model the removal of chromium (VI) has the maximum adsorption capacity with 181.4 mg g^{-1}. Batch sorption to remove chromium (VI) and lead (II) from the tannery effluents was investigated by using different parameters. The sorption efficiency was found to be 75% and 99% for chromium (VI) and lead (II), respectively, present in the tannery effluents. The chemical and structural characteristics of the adsorbents were determined by UV, FT-IR, TGA, DSC, XRD and SEM-EDS analyses.

1. Introduction

The pollutant from the tannery industries produces wide varieties of high strength toxic chemicals. During the chrome tanning process, 40% unused chromium salts are usually discharged in the final effluents, causing a serious threat to the environment [1]. Metal ions in the environment bioaccumulate and are biomagnified along the food chain. One of the important features that distinguish heavy metals from other pollutants is that the former are non-biodegradable. Once metal

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ions enter the environment, their chemical form largely determines their potential toxicity [2,3]. In aqueous phase chromium exits in two oxidation states such as trivalent chromium (i.e., Cr^{3+}, or $Cr(OH)^{2+}$) and hexavalent chromium (i.e., $HCro_4^-$, Cro_4^{2-} or $Cr_2O_7^{2-}$). Chromium (VI) is very toxic to living organisms than Cr(III) [4–6]. Chromium (III) is essential for human nutrition (especially in glucose) and it is relatively innocuous and immobile. Chromium (VI) ions cause epigastric pain, nausea, vomiting, severe diarrhea, hemorrhaging and are nephrotoxic, mutagenic and carcinogenic. Chromium (VI) ions are notoriously mobile in nature because they are weakly bound to the inorganic surface [7,8]. Lead (II) is one of the most toxic heavy metals causing health problems such as behavioral anomaly, learning disabilities and seizures. Low level of lead (II) has been identified with anemia while high level causes severe dysfunction of kidneys, liver, central and peripheral nervous system, the reproductive system and high blood pressure [9]. Therefore the World Health Organization (WHO) recommends the toxic limits of chromium (VI) and lead (II) in waste water to the level of 0.05 mg L^{-1} [10] and 0.0015 mg L^{-1} respectively [11].

Polymers with redox units, being either integral parts of the polymer matrices or attached ones are distinguished by oxydo-reduction chemistry features. Of the redox entities are organometallics such as metallocenes and organics such as pyridinium salts and hydroquinone or catechol [12]. They are usually attached with functional groups of the redox-type either as pendant groups from polymer matrix or being part of the polymer chain. The redox polymers exhibit redox properties, metallic adsorption through their chelating ability [13,14]. Polymeric adsorbents are superior to other solid adsorbents due to their vast surface area, adjustable surface chemistry, and feasible regeneration under mild conditions. Polymers with specific functionalities can be obtained, by either synthesizing new monomers bearing the functional groups capable of interacting with the target metal ions, followed by polymerization, or by converting the groups on the existing polymers or co-polymers with suitable chemical reactions into the desired functional groups. Imidazo and amidoxime functional groups have been incorporated in the polymer backbone to adsorb various metal ions from aqueous solutions [15]. By incorporation of appropriate functional groups into the ion-exchanger matrix, its selectivity for chromium and lead can be enhanced. The catechol groups can form strong hydrogen bonds with other materials and therefore, catechol is widely used to design functional polymers [16]. In the present study, an attempt was made to synthesize redox polymer with polyacrylic acid and was integrated with catechol–hydroquinone. The synthesized redox polymers were used for the adsorption of heavy metals like chromium (VI) and lead (II) from the tannery effluents and the adsorption capacities were compared with the chromium ions in aqueous solution.

2. Materials

All the chemicals were purchased from Merck and Aldrich and were used as received.

2.1. Characterization

The viscometric measurements were performed in dioxane at 30 °C using Cannon Ubbelohde capillary viscometer. The average molecular weights (Mv) were estimated by the standard relation of Mark–Houwink–Sakurada [17]. UV–Vis spectra were recorded using a UV–Vis spectrophotometer, Systronics. Infrared spectra were taken with a Bruker FT-IR. X-ray diffraction measurement was carried out using Diffractometer system XPERT-PRO with Cu Kα radiation (λ=0.154 nm) at the scanning rate of 2°/min. The thermal studies were recorded on SDT Q600 V8.3 build 101 with the heating rate of 10 °C min^{-1} under nitrogen atmosphere. The scanning electron micrographs and EDS of polymer samples have been scanned at 5000 × to 10,000 × magnification at the accelerating voltage of 10 kV with the working distance of 10 mm by FEI Quanta FEG 200 High Resolution SEM-EDS. The concentration of the chromium and lead metal ions of the tannery effluents was estimated through Perkin Elmer Optima 5300 DV ICP-OES at the wavelength of 267.716 nm and 220.353 nm respectively.