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Adsorption behavior of Cr(VI) onto radiation crosslinked chitosan and its possible application for the treatment of wastewater containing Cr(VI)

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Abstract

Adsorption of Cr(VI) onto crosslinked chitosan synthesized by gamma irradiation in the presence of carbontetrachloride has been investigated. The adsorption behavior of crosslinked chitosan (CRC) and its hydrolysis product (CRCH) has been compared with native chitosan. The maximum adsorption of Cr(VI) on crosslinked chitosan occurs at pH 3. The results obtained from equilibrium adsorption studies are fitted in various adsorption models such as Langmuir, Freundlich and Dubinin–Radushkevich (D–R) and the model parameters have been evaluated. Various thermodynamic parameters like H^0, S^0 and G^0 for adsorption of Cr(VI) onto crosslinked chitosan have been estimated. The performance of crosslinked chitosan (CRC and CRCH) under flow conditions have also been studied and the results indicates that radiation crosslinked chitosan can be effectively used for treating wastewater containing Cr(VI). The most important aspect of using crosslinked chitosan for treating the wastewater containing Cr(VI) is that after the Cr(VI) is loaded; the column can be easily regenerated and efficiently reused.

Keywords: Chromium; Gamma radiation; Freundlich model; Dubinin–Radushkevich model; Wastewater

1. Introduction

The toxic heavy metals like copper, mercury, chromium, lead, nickel and cadmium can have serious impact on the aqueous environment, animals and humans. Chromium and its compounds are widely used in plating, leather tanning, dye, cement, and photography industries producing large quantities of toxic pollutants [1]. Chromium can exist in the form of several oxidation states, however, only the trivalent and hexavalent forms are environmentally important [2]. Chromium(III) has been reported to be biologically essential to mammals as it maintains effective glucose, lipid and protein metabolism. While, chromium(VI) can be toxic as it can diffuse as CrO_4^{2-} or $HCrO_4^-$ through cell membranes and oxidize biological molecules [3]. The maximum permissible levels of Cr(VI) in potable and industrial wastewater are 0.05 and 0.25 mg dm^{-3}, respectively [2]. Due to its high solubility, Cr(VI) is very toxic to living organisms compared to Cr(III) [4]. When

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Cr(VI) is ingested beyond the maximum concentration, it can cause health disorders, such as vomiting and hemorrhage [5]. Therefore, treatment of wastewater containing Cr(VI) prior to discharge is essential. Conventional techniques for removing metal ions from wastewater include chemical precipitation, membrane separation, reverse osmosis, evaporation and electrochemical treatment. However the effectiveness of these methods for removing at low concentration is very low. Adsorption is one of the important alternatives available for such situation. The use of polymeric material as an adsorbent for the removal of Cr(VI) is reported in the literature [6–8]. In the recent years, a variety of low cost adsorbent materials have been developed for their capacity to remove toxic metal ions, as documented in a review [9]. These novel adsorbents include a wide range of materials ranging from microbial biomass to byproducts derived from industrial, agricultural and fishery wastes.

Chitin is one such polymer that is extracted from the waste of fishery industry. It is a white, hard, inelastic nitrogenous polysaccharide found in the outer skeleton of insects, crabs, shrimps and other marine animals. Chitin is the second most abundant natural polymer polysaccharide and estimated to produce annually almost as much as cellulose [10]. Chitin is converted into chitosan by alkaline hydrolysis using 50% (w/w) aqueous NaOH solution as shown in Fig. 1. Chitosan has many applications due to the presence of reactive $-NH_2$ group at position 2 and two hydroxyl group at position 3 and 6, respectively, of 2-deoxy-D-Glucose residue. Due to the presence of amino group at position 2 and hydroxyl group at position 3, chitosan forms chelates [11] with almost all the metal ions. Further being a cationic polymer, it adsorbs many negatively charged species from aqueous media. The solubility of chitosan in aqueous acid media is a limiting factor for many such applications. It is therefore necessary to crosslink chitosan to render it insoluble in acid media. Chitosan is generally crosslinked using chemical reagents [12] such as glutraldehyde and epichlorohydrin. Recently we have developed a gamma radiation based method for crosslinking chitosan in the presence of carbon tetrachloride as sensitizer [13]. Application of radiation crosslinked chitosan to treat wastewater containing Cr(VI) is explored and the results obtained are presented in this communication.

2. Experimental

2.1. Materials and chemicals

Chitin was purchased from M/s S.D. Fine chemical, Mumbai, while Chitosan was prepared by hydrolyzing chitin with 50% (w/w) NaOH solution for 2 h. The mixture after hydrolysis was washed with water till free from sodium hydroxide and finally washed with acetone and dried. Methanol and carbon tetrachloride from M/s S.D. Fine chemical, Mumbai were distilled prior to their use. All other chemicals were of analytical grade and were used as received. Double distilled water was used for making solutions. Potassium dichromate was dissolved in water to prepare synthetic wastewater and the pH of the solution was adjusted using H_2SO_4 and NaOH.

2.2. Gamma irradiation

Irradiations were carried out using Co^{60} gamma chamber installed in the Radiation Technology Development Section of BARC having a radiation dose rate of 5 kGy/h, determined using Fricke dosimetry [14].

2.3. Synthesis of crosslinked chitosan

A solution containing 30:65:5 parts by weight of water, methanol and carbontetrachloride was prepared and to which chitosan was added till it is

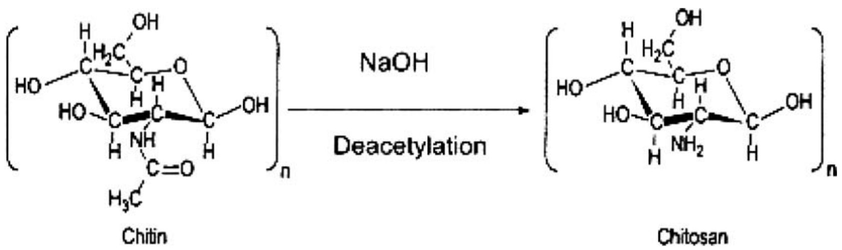

Fig. 1. Deacetylation of chitin into chitosan by alkali hydrolysis.