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Novel chitosan derivative for the removal of cadmium in the presence of cyanide from electroplating wastewater

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Abstract

Chitosan was chemically modified by introducing xanthate group onto its backbone using carbondisulfide under alkaline conditions. The chemically modified chitosan flakes (CMC) was used as an adsorbent for the removal of cadmium ions from electroplating waste effluent under laboratory conditions. CMC was found to be far more efficient than the conventionally used adsorbent activated carbon. The maximum uptake of cadmium by CMC in batch studies was found to be 357.14 mg/g at an optimum pH of 8.0 whereas for plain chitosan flakes it was 85.47 mg/g. Since electroplating wastewater contains cyanide in appreciable concentrations, interference of cyanide ions in cadmium adsorption was found to be very significant. This problem could be easily overcome by using higher doses of CMC, however, activated carbon was not found to be effective even at higher doses. Due to the high formation constant of cadmium with xanthate and adsorption was carried out at pH 8, cations like Pb(II), Cu(II), Ni(II) and Zn(II) did not interfere in the adsorption. Dynamics of the sorption process were studied and the values of rate constant of adsorption were calculated. Desorption of the bound cadmium from CMC was accomplished with 0.01N H_2SO_4. The data from regeneration efficiencies for 10 cycles evidenced the reusability of CMC in the treatment of cadmium-laden wastewater.

Keywords: Cadmium; Electroplating wastewater; Biosorption; Chitosan

1. Introduction

The increasing level of heavy metals in the environment represents a serious threat to human health, living resources and ecological systems [1]. These contaminants must be removed from wastewaters before discharge, as they are considered persistent, bioaccumulative and toxic [2]. Of special technical and economic importance is the selective removal of metals derived from the discharge from electrochemical activities into industrial wastewater. In comparison with other industries, the electrochemical industries uses less water, hence, the volume of wastewater produced is smaller, and the wastewater is highly toxic in nature because of the presence of high concentrations of metals such as copper, nickel, zinc, cadmium and cyanides. The use of cadmium cyanide baths in the electroplating industry generates a strong concern related to environmental impacts due to high cadmium and cyanide toxicity [3]. Adverse health effects due to cadmium are well documented and it has been reported to cause renal disturbances, lung insufficiency, bone lesions, cancer and hypertension in humans [3]. To minimize these environmental impacts, wastewater treatment processes using biosorbents have attracted wide attention in recent years [4–6].

The use of chitosan as biosorbent for heavy metals offers a potential alternative to conventional methods such as chemical precipitation, ion exchange, electrochemical treatments, etc. Chitosan is a hydrophilic, natural cationic polymer and an effective ion-exchanger, with a large number of amino groups which are responsible for the high adsorption property of chitosan. The oxygen atom in the hydroxyl group of the chitosan can be classified as a hard ligand group having less affinity for heavy metals according to the HSAB (hard and soft acids and bases) classification system [7]. If soft ligand groups such as sulfur can be introduced on to the chitosan backbone, it will increase the uptake capacity for many heavy metals because cadmium can be classified as soft acids, which have a strong affinity to soft ligands. Since sulfur has a very strong affinity for most heavy metals, the metal–sulfur complex is very stable in basic

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conditions [8]. The use of materials with surface functional groups, such as xanthate group, shows improved selectivity for the removal of heavy metals in wastewater [9].

For this purpose, we have developed [10] an effective, simple and low cost alternative employing chelating agent with xanthate groups incorporated on chemically modified chitosan flakes (CMC). This modified chitosan can further enhance the metal binding capacities of chitosan. Comparative evaluation of CMC with plain flakes (PF) and activated carbon (AC) was investigated. Influence of the presence of different ions such as: sulfate, chloride, carbonate, cyanide and other cations at various initial concentrations on cadmium sorption by CMC, in batch conditions were studied. The present study also explores the possibilities of recycling the electroplating wastewaters free of cadmium ions. The economic and environmental advantages of recycling and reusing waste make CMC adsorbent an attractive treatment option.

2. Materials and methods

2.1. Materials

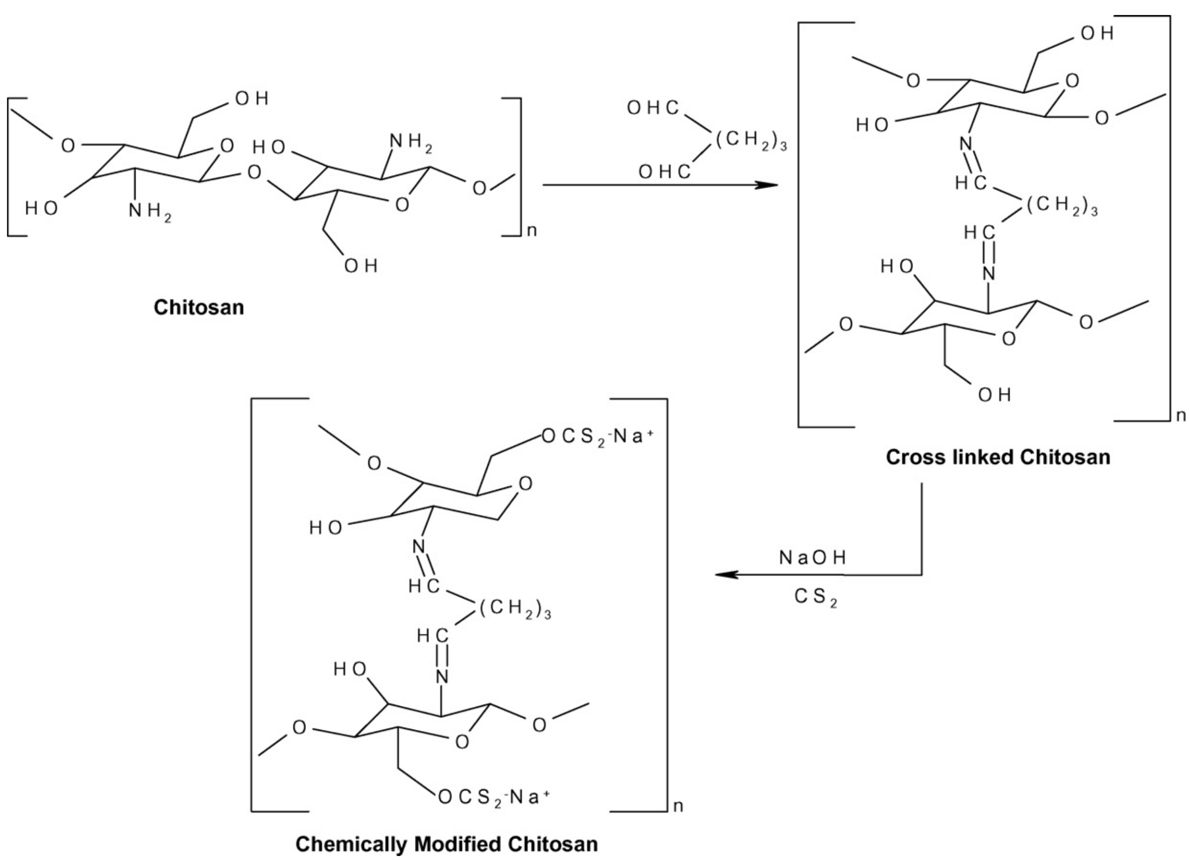
Chitosan flakes was purchased from Sigma Chemicals and used in the present study without any further purification. The degree of deacetylation was reported to be 85% by the manufacturer. Glutaraldehyde and carbondisulfide were purchased from Sigma–Aldrich and used without further purification. Stock solution of Cd(II) was prepared using $Cd(NO_3)_2{\cdot}4H_2O$ (BDH chemicals). All the inorganic chemicals used were analar grade and all reagents were prepared in Millipore milli-Q deionised water.

2.2. Chemical modification of the chitosan flakes (CMC)

Chitosan flakes were cross-linked with glutaraldehyde and chemically modified (Scheme 1) and characterized as described earlier [10]. To obtain 20% cross-linking [11], chitosan flakes (ca. 0.5 g) were suspended in methanol (100 ml), and a 25% aqueous glutaraldehyde solution (0.046 ml, 0.12 mmol) was added. After stirring at room temperature for 6 h, the product was filtered. Cross-linked chitosan flakes (0.5 g) were treated with 25 ml of 14% NaOH and 1 ml of CS_2. The mixture was stirred at room temperature for 24 h. The obtained orange product, cross-linked chemically modified chitosan flakes were washed thoroughly with water, air-dried and used for further experiments.

2.3. Metal concentration analysis

Dissolved cadmium was determined by Analyst 400 Perkin-Elmer Atomic Absorption Spectrophotometer using an air–acetylene burner. The measurements were done at wavelength 228.8 nm using a slit width of 0.7 nm. Experimental samples were filtered using Whatman 0.45 mm filter paper and



Scheme 1. Chemical modification of plain chitosan flakes.