



Preparation and characterization of nano chitosan for treatment wastewaters



M.S. Sivakami^a, Thandapani Gomathi^b, Jayachandran Venkatesan^c, Hee-Seok Jeong^c,
Se-Kwon Kim^{c,*}, P.N. Sudha^{a,b,**}

^a Department of Chemistry, Government Thirumagal Mills College, Gudiyattam, Tamil Nadu, India

^b PG and Research Department of Chemistry, DKM College for Women, Vellore, Tamil Nadu, India

^c Department of Chemistry and Marine Bioprocess Research Center, Pukyong National University, Busan 608-737, Republic of Korea

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ABSTRACT

Chitosan nanorod with minimum particle size of <100 nm was prepared by crosslinking low molecular weight chitosan with polyanion sodium tripolyphosphate and physicochemically characterized (FT-IR, XRD, SEM, AFM, TGA and DSC) for waste water treatment. Its sorption capacity and sorption isotherms for chromium (Cr) were studied. The effect of initial concentration of Cr ions, sorbent amount, agitation period and pH of solution that influence sorption capacity were also investigated. It was found that nanochitosan in the solid state was rod shaped which could sorb Cr (VI) to Cr (III) ions effectively. Based on the Langmuir, the Freundlich and the Temkin sorption isotherms, the sorption capacity of chitosan nanoparticles is very high and the adsorbent favors multilayer adsorption. The kinetics studies show that the adsorption follows the pseudo-second-order kinetics, which infers the transformation of Cr (VI) to Cr (III). From the results it was concluded that nanochitosan is an excellent material as a biosorbent for Cr removal from water.

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1. Introduction

71% of the total surface of earth is water. Most of the water bodies as ponds, lakes, streams, rivers, sea and oceans, have become polluted due to population expansion, haphazard rapid urbanization, industrial and technological expansion, energy utilization and waste generation from domestic and industrial sources. The presence of heavy metals in the environment has been of great concern due to their increased discharge, toxic nature and other adverse effects on receiving waters.

Chromium (Cr) and its compounds are present in the wastewater from electroplating, leather tanning, film and photography, dyes and pigments, textiles, steel fabrication and canning industries [1]. In environmental waters, Cr exists predominantly in two stable oxidation states Cr (III) and Cr (VI) and have contrasting toxicities mobility and availability [2]. Cr (III) is an essential

component having an important role in the glucose, lipid and protein metabolism, while Cr (VI) has a definite adverse impact on living organisms. Cr (VI) is known to have 100-fold higher toxicity than Cr (III) because of its high water solubility, mobility and easy reduction [3]. The United States Environmental protection Agency has laid down the maximum contaminant level for Cr (VI) into inland surface waters as 0.1 mg/L and in domestic water supplies to be 0.05 mg/L. The toxicological effect of Cr (VI) originates from the action of this form itself as an oxidizing agent, as well as formation of free radicals during the reduction of Cr (VI) to Cr (III) occurring in the cell [4]. Research on carcinogenicity of Cr (VI) has focussed on the fact that the free radicals produced inside the cell strongly bind to DNA. Breathing and holding of Cr (VI) containing material can cause perforation of the nasal septum, asthma, bronchitis, pneumonitis, inflammation of larynx and liver and increased incidence of bronchogenic carcinoma [5].

The removal of toxic heavy metal ions from industrial effluents, water supplies and mine waters has received much attention in recent years. Several methods adopted to remove Cr from the industrial wastewater are chemical precipitation, ion exchange, reduction, electrochemical precipitation, solvent extraction, membrane separation, cementation, electrodialysis and adsorption. Among the cited methods, each method has its own limits and in recent years biosorption is recognized as an emerging technique for the treatment of wastewater containing heavy metals

* Corresponding author at: Department of Chemistry and Marine Bioprocess Research Center, Pukyong National University, Busan 608-737, Republic of Korea. Tel.: +82 51 629 7094; fax: +82 51 629 7099.

** Corresponding author at: PG and Research Department of Chemistry, DKM College for Women, Vellore, Tamil Nadu, India. Tel.: +91 9842910157.

E-mail addresses: sivakamiselvakumar2009@gmail.com (M.S. Sivakami), sknkim@pknu.ac.kr (S.-K. Kim), drparsu8@gmail.com, parsu8@yahoo.com (P.N. Sudha).

[6]. The major advantages of biosorption over conventional treatment methods include: low price, high effectiveness, minimization of chemical and/or biological mud, restoration of biosorbent and possibility of metal recovery [7–11].

Some of the biosorbents include chitosan and modified chitosan. Chitosan is a biopolymer of polyaminosaccharide, synthesized from the deacetylation of chitin, consisting of unbranched chains of β -(1, 4)-2-acetoamido-2-deoxy-D-glucose. Chitosan is more useful than chitin since it possesses more number of chelating amino groups and can be chemically modified [12]. Chitosan is an antibacterial, biocompatible, environment friendly, biodegradable material and has great potential for sorption of metal ions due to amino and hydroxyl groups in its chemical structure [13–17]. Compared to traditional micro-sized supports used in separation process, nano-sized adsorbents possess good performance due to high specific surface area, small size and quantum size effect that could make it exhibit higher capacities for metal ions [18]. Investigations reveal that chitin and chitosan are easily processed into gels, membranes, nanofibers, beads, microparticles, nanoparticles, scaffolds and sponges [19]. The present investigation aims to synthesize chitosan nanoparticles by ionic gelation of chitosan and tripolyphosphate and evaluates its sorption capacity for Cr (VI) by varying the operational factors (pH of solution, agitation time, ion concentration and adsorbent concentration) that are responsible for adsorption. This is the first report on sorption property of chitosan nanorod in the conversion of Cr (IV) to Cr (III). For this, the equilibrium data were fit to the Langmuir, the Freundlich and the Temkin sorption isotherms.

2. Materials and methods

2.1. Chemicals and reagents

Chitosan (deacetylation 92% and MW 120,000) was procured from India Sea Foods, Cochin, Kerala, India. Sodium tripolyphosphate, potassium dichromate and acetic acid of AR grade were used without any further purification.

2.2. Preparation of chitosan nanoparticles

The method adopted is as reported by Tang et al. [35]. 20 mg chitosan was dissolved in 40 ml of 2.0% (v/v) acetic acid. 20 ml of 0.75 mg/ml sodium tripolyphosphate was dropped slowly with stirring. Chitosan nanoparticles as a suspension were collected and stored in deionised water. Supernatant was discarded and nanochitosan was air dried for further use and analysis.

2.3. Characterization of chitosan nanoparticles

2.3.1. Fourier transform infrared spectroscopy (FT-IR) analysis

FT-IR analysis of chitosan and chitosan nanoparticles were carried out in the range between 4000 and 375 cm^{-1} using Thermo Nicolet AVATAR 300 FTIR spectrometer using KBr pellet method.

2.3.2. X-ray diffraction (XRD) analysis

In X-ray diffraction technique (XRD), X-ray diffraction profiles of chitosan and chitosan nanoparticles were recorded by Bruker, Germany powder X-ray diffractometer, model D8 Advance, source 2.2 kW Cu anode, Ceramic X-ray tube. The relative intensities were recorded within the range of 10–90° (2θ) at a scanning rate of 5° min^{-1} .

2.3.3. Thermogravimetric (TGA) and differential thermogravimetric (DTG) analysis

Thermogravimetric (TG) analysis and differential thermogravimetric of chitosan and chitosan nanoparticles were carried

out on a SDT Q600 V8.0 Build 95 instrument at a heating rate of 10 °C/min in nitrogen atmosphere. The weight losses at different stages were analyzed. DSC curves of the samples were obtained using a NETZSCH DSC 200PC in a Al pan, pierced lid in the N_2 atmosphere at a heating rate of 10 °C/min. The results were recorded and analyzed.

2.3.4. Size and morphology of chitosan nanoparticles

Chitosan nanoparticles were analyzed for its particle size and distribution using Nanotracer analyzer 6Hx4Wx15D, Model-Nanotracer 150 with a measuring range of 0.8–6500 nm (10^{-9} m). Chitosan nanoparticles were cut into pieces of various sizes and wiped with a thin gold–palladium layer by a sputter coater unit (UG-microtech, UCK field, UK) and the morphology of nanoparticles was analyzed with a Cambridge stereoscan 440 scanning electron microscope (SEM, Leica, Cambridge, UK). AFM was used for visualization of chitosan nanoparticles rough nature to facilitate adsorption of heavy metals. AFM imaging was performed using CONTR, EZ-2-AFM analysis.

2.4. Sorption experiments

Sorption experiments were conducted in 250 ml conical flasks containing 100 ml of various concentrations of Cr (VI) solution using accurately weighed chitosan nanoparticles. The flasks were agitated in an orbit shaker at room temperature. The effect of contact time on the sorption capacity of sorbent was studied in the range 1–5 h at an initial Cr concentration of 200 mg/L. Effect of initial pH on the sorption capacity of sorbent for Cr (VI) was studied by varying solution pH from 3 to 9 at the sorbent dosage of 1 g/100 ml for 1 h contact time using 200 mg/L initial Cr concentration. The solution pH was adjusted with dilute HCl or NaOH solution. The effect of sorbent dosage was studied from 1 g to 5 g for 1 h contact time. Adsorption isotherms were studied at different initial Cr concentrations viz., 75, 125, 250, 500, 750, 1000 mg/L at room temperature. The data were fitted into the Langmuir, the Freundlich and the Temkin isotherm models.

2.5. Analysis of Cr (VI) ions

The Cr sorbent adsorbent was dried and preserved. For desorption, the Cr-sorbed adsorbent was shaken with dilute hydrochloric acid for one hour and filtered. The filtrate was analyzed for the oxidation state of Cr using UV–visible spectrophotometer, Model Hitachi U-2800 in the wavelength ranges 190–1100 nm.

3. Results and discussion

3.1. General discussion

Chitosan, a biopolymer is biodegradable, biocompatible, non-toxic, economic and having great potential over wide range of application, which was due to the presence of $-\text{OH}$ and $-\text{NH}_2$ groups. Being a good adsorbent for the removal of heavy metals from wastewater, it also has some disadvantages. Poor mechanical properties and solubility in low pH limit its application. To overcome these limitations chitosan needs modification. We modified chitosan into chitosan nanoparticles with rod shape by ionic gelation method, which have more advantages over chitosan. Due to this modification to nano size the amorphous nature increases and acts as a better adsorbent.

(A) Chitosan solution, (B) chitosan film, (C and D) chromium sorbed nanochitosan wet condition and dried condition have been shown in Fig. 1(I). It was found that chitosan films are present in the form of off white color, whereas, the treated chitosan are found in

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