



Chemical modification of cellulosic biopolymer and its use in removal of heavy metal ions from wastewater



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ABSTRACT

Use of biological macromolecules for wastewater remediation process has become the topic of intense research mostly driven by growing concerns about the depletion of petroleum oil reserves and environmental problems. So in view of technological significance of cellulosic biopolymers in various fields, the present study is an attempt to synthesize cellulosic biopolymers based graft copolymers using free radical polymerization. The resulting cellulosic polymers were characterized by Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermogravimetric (TGA) analysis. Furthermore, modified cellulosic biopolymer was used in removal of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} toxic metal ions from wastewater. The effects of pH, contact time, temperature and metal ions concentration were studied in batch mode experiments. Langmuir and Dubinin–Radushkevich (D–R) models were used to show the adsorption isotherm. The maximum monolayer capacity q_m calculated using Langmuir isotherm for Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} metal ions were 1.209, 0.9623, 1.2609 and 1.295 mmol/g, respectively. The thermodynamic parameters ΔH° and ΔG° values for metal ions adsorption on modified cellulosic biopolymer showed that adsorption process was spontaneous as well as exothermic in nature.

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1. Introduction

Cellulose and its derivatives are the most abundant natural biomacromolecules, which are used in a number of advanced applications, such as in paper, packaging, biosorption, biomedical and in preparation of biocomposites. Among the various application of cellulose and its derivatives in different fields, the use of cellulosic biomacromolecules for wastewater remediation process has become the topic of intense research mostly driven by growing concerns about the depletion of petroleum oil reserves and environmental problems. Heavy metal ions pollution is one of the most important environmental problems being faced by the modern day society. The rapid industrialization and other mining activities have resulted in increased heavy metal concentrations in surface and ground waters. The pollution of water with heavy metal ions is considered dangerous due to their high toxicity and non-biodegradability [1]. Further, heavy metal ions can be accumulated through the food chain even at low concentrations, leading to serious problems on aquatic, animal, plant and human health [2].

The harmful and negative effect of heavy metals on living beings and ecosystem has forced the scientific community across the globe to devise new methods to avoid these ill effects. Various conventional methods such as chemical precipitation, filtration, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon and evaporation have been suggested for removal of metal ions from aqueous solution [3]. However, most of these methods are ineffective and also produce large quantity of sludge. Ion exchange, membrane technologies and activated carbon adsorption process are extremely expensive and hence cannot be used at large scale [4,5]. However in recent years, cellulosic biofibers are highly efficient, low cost and renewable source of biomass which can be exploited for wastewater remediation. Further these biofibers can be chemically modified for better efficiency and multiple reuses to enhance their applicability at large scale. Chemical modification of cellulosic biofibers is carried out to achieve efficient adsorption capacity for heavy metal ions [6–8]. Chemical modification by graft copolymerization of vinyl monomers onto cellulosic biofibers provides large number of functional groups which improves the adsorption capacity of cellulosic fibers significantly.

Among these cellulosic biomasses, cellulosic okra fiber is another potential agriculture waste biomass which can be used as adsorbent for wastewater treatment. Okra fiber is an agricultural

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waste biomass principally composed of cellulose, hemicellulose and lignin. In continuation with our previous efforts, the current work presents the graft copolymerization of cellulosic okra fibers with acrylonitrile and methacrylic acid binary vinyl monomer is an effort to increase the graft yield as compared to grafting with single acrylonitrile monomer [9]. The structures of the modified cellulosic fibers were confirmed through FT-IR, SEM, TGA and X-ray diffraction techniques. Further graft copolymerized okra fibers have been used for removal of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} heavy metal ions from wastewater. The adsorption parameter including effects of pH, contact time, metal ion concentration and temperature on adsorption were also investigated.

2. Experimental

2.1. Materials

Okra cellulosic fibers were extracted from stem of okra plant and made free from impurities by the method described earlier in the literature [9]. Acrylonitrile (AN) and methacrylic acid (MAA) of 99% purity supplied by CDH were used as vinyl monomers. Hydrogen peroxide (H_2O_2) supplied by Qualigens fine chemicals and ascorbic acid (Asc) supplied by (E-Merck, chemicals limited, Mumbai, India) were used as received. All other chemicals were of analytical grade and used as received without further purifications. For metal adsorption experiments, the stock solutions of Cu(II), Zn(II), Cd(II) and Pb(II) were prepared by dissolving an accurate quantity of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; Merck India), zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; Loba Chemicals) and cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; Qualigens fine chemicals) and lead nitrate ($\text{Pb}(\text{NO}_3)_2$; Merck India) in double distilled water.

2.2. Synthesis of poly(acrylonitrile-co-methacrylic acid)-g-cellulosic okra polymers

Free radical induced graft copolymerization synthesis onto cellulosic fibers with acrylonitrile (AN) and methacrylic acid (MAA) was carried out by immersing them in a precise amount of distilled water for 24 h. A known amount of ascorbic acid dissolved in definite amount of hydrogen peroxide was added to the reaction mixture containing 0.5 g of fibers. The optimized concentration of ascorbic acid and hydrogen peroxide were taken $3.2 \times 10^{-2} \text{ mol/dm}^3$ and $1.61 \times 10^{-1} \text{ mol/dm}^3$, respectively, as reported in the literature [9]. The grafting of AN/MAA vinyl monomers onto cellulosic fibers has been investigated at different feed molarities ranging from 0.3 to 1.0 mol/dm^3 at a fixed mole fraction of AN monomer ($f_{\text{AN}} = 0.4$). The ratio of mole fraction of AN/MAA in the grafting is 0.4/0.6, respectively. The comonomer mixture was then added drop wise to the reaction kettle which was stirred for one hour with the help of electrically operated magnetic stirrer maintained at a constant temperature of 55 °C. Finally when the reaction time was over, product was filtered and washed with double distilled water. To ensure complete removal of homopolymers, the crude was Soxhlet extracted for 24 h with dimethylformamide and acetone. The graft copolymers free from homopolymers were then dried in a hot air oven at 60 °C to a constant weight. The grafting parameters percent graft yield (P_g) and percent graft efficiency (P_e) were calculated by following expression:

$$\text{Percent graft yield } (P_g) = \frac{w_2 - w_1}{w_1} \times 100 \quad (1)$$

$$\text{Percent graft efficiency } (P_e) = \frac{w_2 - w_1}{w_m} \times 100 \quad (2)$$

where w_1 , w_2 and w_m are the weight of raw and grafted cellulosic fiber, respectively.

The grafted okra fibers were then ball milled in ball mill apparatus, so that the average particle size of the fibers was reduced to 60 μm which was confirmed by SEM-EDX study.

2.3. Amidoximation of poly(acrylonitrile-co-methacrylic acid)-g-cellulosic okra fibers

2.0 g of poly(AN + MAA) vinyl monomer grafted cellulosic particle fibers were treated with an aqueous solution of hydroxylamine hydrochloride [10]. The pH 10 of solution was adjusted by adding sodium carbonate. The ratio of hydroxylamine hydrochloride and sodium carbonate in reaction mixture was 1:0.75 by weight, respectively. The reaction mixture was taken in a 500 mL round bottom flask to which 100 mL of deionized water was added and sealed. The reaction was carried out at 70 °C for 90 min. The product was filtered, washed with deionized water for several times in order to remove the remaining traces of salts and finally dried at 60 °C. This dried chemical product was further used as adsorbent for adsorption studies.

2.4. Characterization of chemically modified fibers

The surface morphologies of cellulosic fiber before and after graft copolymerization were studied using FEI Quanta 450 SEG scanning electron microscopy machine at very high magnification. Functional groups in cellulosic fiber before and after chemical modification were determined by the FTIR Spectrometer (Perkin-Elmer spectrophotometer) in the transmittance (%) mode with a scan resolution of 4 cm^{-1} in the range 4000–500 cm^{-1} .

Crystallinity index of the raw and chemically modified samples were studied through X-RD analysis using X-ray powder diffractometer (Philips 1710 X-ray diffractometer). The sample was scanned from 5 to 50° in step of 2°/min. Thermogravimetric analysis of the raw and chemically modified samples was performed using a Linseis L81-II at a heating rate of 10 °C/min in temperature range of 30 to 800 °C. The pH measurements of all aqueous samples were performed following standard methods with pH meter manufactured by Eutech Instruments.

2.5. Adsorption equilibrium experiments

Adsorption data such as kinetic, thermodynamic and adsorption isotherm was obtained by batch techniques. The experiments were conducted in 250-mL Erlenmeyer flasks containing 0.050 g of adsorbent and 50 mL of metal ion solution in varying concentrations from 100 to 1000 mg/L. The flasks were shaken at an agitation speed of 150 ± 2 rpm at electrically thermostated reciprocating shaker for different time intervals. The metal ion concentration before and after the adsorption process was calculated by the method reported in the literature as follow. The metal ion concentration of Cu^{2+} in the filtrate was determined by direct titration with standard EDTA solution (1 mmol/L) at pH 10 using murexide as an indicator [11]. The concentration of Zn^{2+} , Cd^{2+} and Pb^{2+} ions was determined by back titration of standard EDTA solution (3 mmol/L) with aqueous Mg^{2+} standard solution (2.0 mmol/L) at pH 10 using Erichrome Black T as indicator [11,12]. All experiments were repeated thrice and mean values were used. The adsorption amount (q) was calculated according to Eqs. (4) and (5):

$$q = \frac{(C_0 - C_e)}{W} \times V \quad (3)$$

where W is the weight of the adsorbent in gram (g), V is the volume of solution in litre (L) and C_0 and C_e are the initial and equilibrium concentrations of metal ions in solution. The pH of metal solutions was adjusted with 0.1 M HNO_3 and 0.1 M NaOH .

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