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Application of vinyl monomers functionalized cellulosic biopolymer for removal of dissolved toxic metal ions from polluted water samples

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ABSTRACT

In the present study, a binary vinyl monomer mixture of acrylonitrile (AN) and acrylamide (AAm) was graft copolymerized onto cellulosic fibers using ascorbic acid and hydrogen peroxide as redox initiator. The grafted fibers were further reacted with aqueous solution of hydroxylamine hydrochloride at pH 10.0 to convert them into amidoxime derivative. These resulting functionalized cellulosic fibers were characterized by various techniques such as FT-IR, TGA, and SEM studies. The functionalized fibers were used for removal of toxic metal ions from aqueous solution through adsorption process. The adsorption process follows pseudo-second-order kinetics and relative adsorption rate of various metal ions were found in the order of $Pb^{2+} > Zn^{2+} > Cd^{2+}$. Langmuir, Freundlich and Dubinin–Radushkevich models were used to show the adsorption isotherm. Langmuir model fits better with the equilibrium data. The maximum monolayer capacity q_m calculated using the Langmuir isotherm for Zn^{2+}, Cd^{2+} and Pb^{2+} metal ions were 55.72, 106.72 and 200 mg/g respectively. From thermodynamic parameters ΔH° and ΔG° values were obtained. The adsorption process has been found to be exothermic in nature.

1. Introduction

Among various types of pollution, water pollution has become a major cause of concern for the sustenance of life. Contamination of soil, groundwater and surface water with toxic heavy metal ion is causing health related problems to both human being and marine life [1,2]. Heavy metal ions such as copper, nickel, zinc, chromium, cadmium and lead which are dangerous pollutants of nature are being constantly discharged into the environment/water bodies by various industries such as surface finishing industry, fertilizer, pesticide, metallurgy and leather industries etc. [3]. In order to reduce concentration of these toxic metal ions in water bodies various methods like precipitation, ion exchange, adsorption, membrane processes, electrolytic methods have been used which are quite expensive in nature [4]. Among various methods, adsorption has been found to be quite effective process for the removal of heavy metal ions from aqueous solution [5]. Recently low cost adsorbents such as cellulosic fibers have attracted the attention of scientists for effective removal of toxic metal ions [6,7].

Cellulosic fibers represent a huge reservoir of renewable biomass with an annual reproduction estimated to 18×10^{10} ton [8]. Adsorption on cellulosic fibers has been an attractive approach due to their low cost, high efficiency, formation of low sludge and regeneration of adsorbent [9]. However their adsorption capacity is quite low as the hydroxyl groups present are rather involved into intermolecular hydrogen bonding than into interaction with toxic metal ions [7]. In order to enhance their adsorption capacity, chemical modification of cellulosic fibers thorough graft copolymerization has been found to be an effective technique [10–13]. Further, introduction of amidoxime groups on grafted cellulose and cellulosic fiber has been found to be more effective than grafted fiber in removal of metal ions from aqueous solution [14,15]. Various cellulosic biomass including banana stem fibers, peanut shells, cocoa pod husk, corn cob, bamboo leaf powder and other lignocellulosic waste materials such as rice husks, spent grain, sawdust, sugarcane bagasse, fruit wastes have been used as adsorbents in wastewater treatment applications [16–21].

Among various types of natural biomass, cellulosic okra fiber is a potential biomass which can be used as adsorbent for wastewater treatment. Okra fiber is an agricultural waste biomass principally composed of cellulose, hemicellulose and lignin. Okra fibers are extracted from the stem of a plant of the Malvaceae family (*Abelmoschus esculentus*) which is found in tropical, subtropical and warm temperate regions around the world. As an extension of our previous work, this study presents the graft copolymerization of cellulosic okra fibers with binary vinyl monomer mixture of acrylonitrile (AN) and acrylamide (AAm) [22]. Further these functionalized okra fibers have been used for removal of Zn^{2+}, Cd^{2+}

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and Pb^{2+} heavy metal ions from polluted water sources. The adsorption parameters including effects of time, metal ion concentration and temperature on adsorption have been investigated.

2. Experimental

2.1. Materials and methods

Okra fibers extracted from stem of okra plant were made free from impurities by the method earlier reported in the literature [23]. Acrylonitrile (AN) and acrylamide (AAm) 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. The other chemicals and solvents used were of analytical grade and used without further purification. For metal adsorption experiments, the stock solutions of Zn(II), Cd(II) and Pb (II) were prepared by dissolving a fixed amount of zinc nitrate (Zn $(NO_3)_2.6H_2O$; Loba Chemicals), cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$; Qualigens fine chemicals) and lead nitrate ($Pb(NO_3)_2$; Merck, India) in double distilled water.

2.2. Graft copolymerization of cellulosic okra fibers

The graft copolymerization of cellulosic fibers was carried out by free radical polymerization of a binary mixture of acrylonitrile (AN) and acrylamide (AAm) monomers onto it. Prior to grafting with binary vinyl monomers, various reaction parameters such as reaction time, temperature, concentration of ascorbic acid, hydrogen peroxide and acrylamide concentration were optimized for graft copolymerization of principal (acrylonitrile) monomer onto okra fiber. The results of optimization of different reaction parameters have been reported earlier [22]. Then 0.5 g of fiber was

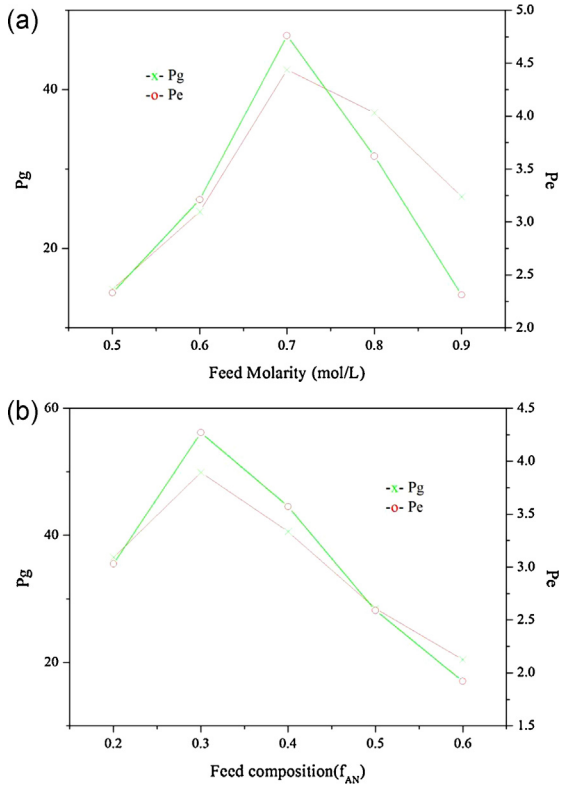
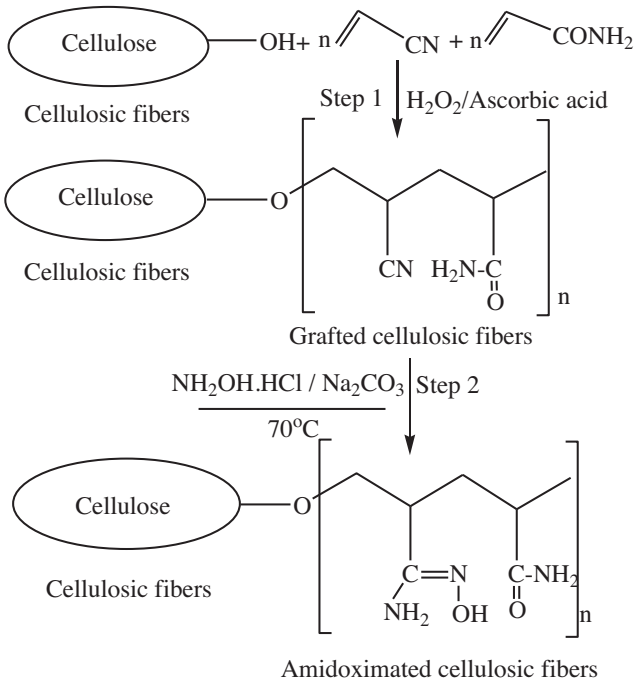


Fig. 1. (a) Effect of feed molarity on percent graft yield and percent efficiency. (b) Effect of feed composition on percent graft yield and percent efficiency.



Scheme 1. Reaction scheme for the modification of okra cellulosic fiber.

taken in a reaction kettle to which known amount of ascorbic acid dissolved in definite amount of hydrogen peroxide was added. Comonomer mixture was then added drop wise into above reaction mixture. The mole fraction of acrylonitrile (f_{AN}) in the reaction mixture was maintained at 0.40. The reaction was stirred at a constant temperature of 55 °C for 1 h. The grafting reaction was then stopped by adding 10 mL of hydroquinone solution (3%). To ensure complete removal of homopolymer formed during reaction, the grafted crude was Soxhlet extracted for 24 h with dimethylformamide/acetone. The graft copolymer free from homocopolymer was then dried in a hot air oven at 60 °C to a constant weight. 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 study. The percent graft yield (P_g) and percent graft efficiency (P_e) were calculated by following expressions:

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

$$\text{Percent graft efficiency}(P_e) = \frac{B-A}{C} \times 100 \quad (2)$$

where A and B are the weight of raw and grafted cellulosic fiber respectively. C represents the weight of monomer.

2.3. Synthesis of amidoximated derivatives of graft copolymerized fibers

2.0 g of graft copolymerized okra particle fibers was treated with an aqueous solution of hydroxylamine hydrochloride at pH 10 [24]. The pH 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 then taken in a 250 mL Erlenmeyer 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 and washed with deionized water for several times in order to remove the impurities and finally dried at 60 °C. This dried product was further used for adsorption studies.