Journal of Environmental Chemical Engineering 3 (2015) 1038–1046

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Preparation and application of grafted *Holarrhena antidycentrica* fiber as cation exchanger for adsorption of dye from aqueous solution

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ARTICLE INFO

Article history:
Received 14 August 2014
Received in revised form 23 February 2015
Accepted 3 March 2015
Available online 9 March 2015

Keywords:
Cation exchanger
Methylene blue
Dye removal
Graft copolymerization
Thermal stability

ABSTRACT

Present investigation deals with the removal of methylene blue from waste water using *Holarrhena antidycentrica* cellulose based cation-exchanger. Initially hydroxyethylmethacrylate was graft copolymerized onto *H. antidycentrica* cellulose and was converted into cation exchanger through phosphorylation. On optimization of different reaction parameters maximum graft yield obtained was 632.0%. Characterization of the synthesized samples was done by FTIR, SEM–EDX and XRD techniques. Thermal stability of samples was investigated through TGA/DTA/DTG techniques. Dye removal study was done in terms of contact time, initial concentration of dye and dose of cation exchanger. Ion-exchanger was found to be highly efficient for removal of methylene blue with maximum removal of 85%. The results showed that ion exchanger could be employed as effective and low cost eco-friendly material for removal of dyes and color from aqueous solution.

Introduction

Mankind has used dyes for thousands of years. Synthetic dyes are extensively used in different fields like paper industries, food industries, leather industries, agriculture research, ground water tracing and many more. There are more than 100,000 commercial dyes used for different applications having estimated production of 7×10^5–1×10^6 t year^{-1} [1]. Extensive application of synthetic dyes can cause considerable environmental pollution and are dangerous to the health of living organisms due to their toxic, mutagenic, allergic and carcinogenic nature. High volumetric discharge of these toxic products makes it necessary to develop various technologies for the effective removal of dyes from wastewater. Different technologies and processes like biological treatments [2], chemical and electrochemical techniques [3], membrane processes [4], advanced oxidation processes [5], and adsorption procedures [6–8] are widely used for removing dyes from industrial waste. Each method has own set of advantages and disadvantages when used for different applications. Removal of contaminants by adsorption using sorbents is one of the most popular methods as this method shows high removal efficiency as well as offers potentially economical and ecological way for water decontamination [9]. Adsorption is a well-known equilibrium separation process in which adsorbents used may be of mineral, organic or biological origin. Silica beads [10], activated carbons [11,12], clays [13], agricultural wastes [14] and polymeric materials [15] are well developed for removal of dyes from water. Recently, there is renewed research interest in development of cheaper and effective adsorbents based on natural polymers to replace costly materials and processes. Natural polymers, particularly, polysaccharides represent promising candidates as adsorbents due to their particular structure, chemical stability and high reactivity as well as selectivity towards aromatic compounds owing to presence of reactive functional groups like hydroxyl, amino and carboxyl in polymer chains, fast adsorption kinetics and appealing diffusion properties. Moreover, polysaccharides are preferred due to their abundance availability, renewability and biodegradability. Different polysaccharides such as chitin, starch, cyclodextrin and their derivatives have been studied as adsorbents for dye removal from waste water [16–18].

Adsorption capacities of natural polymers can be enhanced by different chemical modifications out of which graft copolymerization of different functional groups onto polymer backbone is promising one. Grafted cellulosic fibers have good selectivity, favorable physicochemical stability, adjustable functionality, enhanced surface area porosity and structural diversity. Moreover, graft copolymerization increases the density of adsorption sites

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Abbreviations: HaC, *Holarrhena antidycentrica* cellulose fiber; HaC-g-poly (HEMA), *Holarrhena antidycentrica* cellulose graft poly(HEMA); HaC-g-poly (HEMA)-IE, *Holarrhena antidycentrica* cellulose graft poly(HEMA)ion exchanger.

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http://dx.doi.org/10.1016/j.jece.2015.03.001

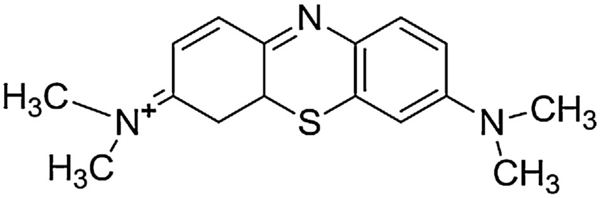

Fig. 1. Structure of methylene blue.

and thereby sorption selectivity for the target metal and dyes. Graft copolymerization of carboxyl, hydroxyl, ammine and sulphur compounds has been reported on different natural backbones [19–23].

Methylene blue (MB) is a heterocyclic aromatic organic compound (Fig. 1). It has been used widely in different fields of biology and chemistry. MB is one of the highly used dyes in printing industries as stabilizer and as indicator in chemical analysis.

Present investigation deals with development of novel cation-exchanger by graft copolymerization and phosphorylation of *Holarrhena antidycentrica* cellulose (HaC) fiber for removal of methylene blue from aqueous solution. Graft copolymer of cellulosic fiber was developed using hydroxyethylmethacrylate as monomer through free radical polymerization. Graft copolymer and cation exchanger was characterized by FTIR, SEM–EDX and XRD studies. Thermal stability was investigated by TGA/DTA/DTG. Utility of cation- exchange was studied for removal of methylene blue from aqueous solution.

Experimental

Material and methods

Holarrhena antidycentrica (Ha) fiber was collected from the hilly region of district Kangra, Himachal Pradesh, India. Fiber was purified through soxhlet extraction in acetone for 72 h. Hydroxyethyl methacrylate (HEMA, SD Fine Chemicals) was purified by vacuum distillation at 0.5 mm of Hg at 85 °C. Ferrous ammonium sulphate (FAS) was purchased from SD Fine Chemicals and recrystallized from hot water. Potassium persulphate (KPS, SD Fine Chemicals) was used as received. Phosphorous oxychloride and methylene chloride used were of analytical grade. Methylene blue was supplied by E-Merk Chemicals.

Extraction of cellulose from the H. antidycentrica fiber

H. antidycentrica fiber was defatted by refluxing in acetone for 72 h. Fiber was crushed and digested with sodium chloride maintaining fiber to liquid ratio of 1:1.50 for 4 h at 65 °C. pH of solution was lowered to 4.0 by adding acetic acid. Fiber was repeatedly washed with water to ensure removal of lignin and water soluble organic components. The resulting fiber was treated with 5% sodium bisulphite solution. Finally, washing was done with water and dried in oven at low temperature (45 °C) to ensure the moisture content of 5–10% (Eq. (2)) [24].

Graft copolymerization

The *Holarrhena antidycentrica* cellulose fiber (HaC) was activated by immersing 0.5 g of fiber in 100 mL of distilled water for 24 h. A definite molar ratio of initiator FAS-KPS was added and reaction was carried out at definite temperature for specific period of time. Homo-polymer was removed by extraction with DMF. Graft copolymer was dried at 50 °C to get constant weight. Percentage graft yield (Pg) was calculated as per the method reported elsewhere (Eq. (3)) [25].

Synthesis of ion exchanger [HaC-g-poly(HEMA)-IE]

Ion exchanger was prepared by phosphorylation of HaC-g-poly (HEMA) with phosphooxy chloride in pyridine. The reaction was performed by refluxing reaction mixture at 115 °C for 2 h. Product obtained was repeatedly washed with water, 0.1 N HCl and methanol to remove traces of pyridine and was dried in hot air oven. The exchanger was converted into H^+ form by treating with 1 mole HNO_3 for 24 h with occasional shaking and intermittently replacing the supernatant solution with fresh acid. The excess of the acid was removed after several washing with DMW. The particle size of the range (~125 μm) was obtained by sieving (Eq. (3)) [26].

Ion exchange capacity of cation exchanger

Ion exchange capacity of HaC-g-poly(HEMA)-PO_4^{2-}2 H^+ was determined with respect to different alkali and alkaline earth metal ions. Glass column having an internal diameter (i.d.) ~1 cm was fitted with glass wool support at the bottom. The bed length was approximately of 1.50 cm. 1.0 g of ion-exchanger was equilibrated with 1.0 mol dm^{-3} solution of different alkali and alkaline earth metal chlorides. Flow rate was maintained at ~0.5 mL min^{-1} and effluent was titrated against standard 0.1 mol dm^{-3} NaOH solution using phenolphthalein indicator [27].

Characterization

FTIR spectra were recorded with Agilent Carry 630 Fourier transform infrared (FTIR) spectrometer with resolution 8 cm^{-1} with sample scans 32 using KBr pellets. SEM–EDX studied of HaC, graft copolymer and cation-exchanger was carried out using FEI Quanta 200 microscope for morphological and elemental analysis of the samples. TGA, DTA and DTG studies were carried-out in the temperature range of 50° –700 °C at a heating rate of 10 °C min^{-1} on TG/DTA 6300, SII EXSTAR 6000. Crystalline studies of the samples were performed on X-ray diffraction instrument (Bruker D8, USA) under ambient conditions using Cu-Kα (1.5418 Å).

Dye adsorption studies of cation exchanger

Adsorption studies were carried-out using 50 mL of methylene blue solution maintained at a constant temperature to study the effect of initial concentration of dye, contact time and dose of the cation exchanger. Experiments were performed at concentrations of 2, 4, 6, 8 and 10 mg L^{-1} of dye using 100–600 mg of cation exchanger at 7.0 pH and 25 °C temperature to attain equilibrium. The extent of adsorption was determined at different time intervals during adsorption process. Each experiment was repeated three times. Dye concentration was determined by UV spectrophotometer at λ_{max} 664 cm^{-1}. The calibration curve was plotted in order to calibrate the instrument to find-out the concentration of unknown samples. Percentage of dye removal was calculated using the Eq. (1) [28]:

$$\%\text{Dyeremoval} = \left[\frac{(C_0 - C_{eq})}{C_{eq}}\right] \times 100 \quad (1)$$

where C_0 and C_{eq} are the initial and equilibrium concentration of dye in mg L^{-1}.

Results and discussion

Graft copolymerization

Reaction parameters were found to play a significant role to achieve the maximum graft yield. Maximum grafting was achieved by optimizing different reaction conditions such as reaction