International Journal of Biological Macromolecules 104 (2017) 1578–1585

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Adsorption and kinetic studies on the removal of chromium and copper onto Chitosan-g-maliec anhydride-g-ethylene dimethacrylate

M.R. Gopal Reddi[a], T. Gomathi[b], M. Saranya[b], P.N. Sudha[b,*]

[a] Department of Chemistry, Bharathiar University, Coimbatore 641 046, Tamilnadu, India
[b] PG and Research Department of Chemistry, D.K.M College for Women, Vellore 632 001, Tamilnadu, India

ARTICLE INFO

Article history:
Received 26 November 2016
Received in revised form 12 January 2017
Accepted 31 January 2017
Available online 4 February 2017

Keywords:
Graft polymerization
Chitosan-g-MA
Ethylene dimethacrylate
Adsorption

ABSTRACT

The present work was designed to remove toxic metals chromium and copper using the double grafted copolymer Chitosan-g-Maleic anhydride-g-ethylene dimethacrylate. The graft copolymer was synthesized through chain polymerization reaction using ceric ammonium nitrate as the initiator. Prepared Chitosan-g-Maleic anhydride-g-ethylene dimethacrylate was used in order to remove the heavy metals chromium and copper from aqueous solutions of 200 ppm/L concentration proceeding batch adsorption process by varying the parameters such as adsorbent dose, contact time, pH and initial concentration of the metal solution. The experimental data were equipped with isotherm models such as Langmuir and Freundlich and pseudo-first order and pseudo-second order kinetics. The calculated results revealed that the adsorption favours Freundlich isotherm and follows pseudo-second order kinetics.

1. Introduction

Industries discharge massive amounts of most toxic pollutants waste into the water system. The main source of water pollution can be attributed to the discharge of untreated waste, dumping of industrial effluent and run-off from agricultural fields. Rapid industrial growth and urbanization is increasing the use of synthetic substances that have a serious impact on our freshwater bodies. The effects of water pollution are not only devastating to people but also to animals, fish and birds. Polluted water is unsuitable for drinking, recreation, agriculture and industry. It diminishes the aesthetic quality of lakes and rivers. More seriously, contaminated water destroys aquatic life and reduces its reproductive ability. Eventually, it is a hazard to human health. Nobody can escape the devastating effects of water pollution.

Heavy metal ion contamination of water sources is hazardous to plants, animals and microorganisms and can be carcinogenic to mankind [1,2]. The metal contamination has increased public concerns because of their toxicities in relatively low concentration and tendency to bioaccumulation [3,4]. Heavy metals are non biodegradable and tend to accumulate in living organisms, resulting in deterioration of public health and causing various diseases and disorders [5–9]. The removal of heavy metal ions from drinking water is a real challenge due to their trace quantities, formation of complexes with natural organic matter, and toxic effect even at low concentrations [10,11]. The improper disposal of these heavy metals can pose serious environmental problems [12]. In view of this, environmental organizations and industries are researching new methods and techniques for controlling toxic waste and minimizing their effects or even eliminating the environmental impact [13].

Many separation methods like chemical precipitation, reverse osmosis, ion exchange and carbon adsorption have been reported to remove metal ions from wastewater [4,14]. But these methods have one or the other disadvantages. For last three decades, adsorption technique, ion exchange and chelation by chelating polymers especially biopolymers have widely been used for metal ion removal because of their advantages over conventional methods. These advantages include economic and environmental like their low cost, availability, reusability, easy separation, higher adsorption capacities, selectivity, ease of operation, and high removal efficiency [4,14–16]. Adsorption is the technique that not only can remove even trace quantities of metal ions from water but also is also highly selective. Detailed studies for the removal of heavy metal adsorption involving equilibrium and kinetic studies and the effects of various factors like temperature, pH and surface area have been reported [17].

Biopolymers like chitosan have been extensively studied because of their interactions with metal ions. These bioadsorbents in native form and chemically modified forms have been effectively used for separation of heavy metal ions from industrial wastewater. It can also bind toxic metal ions, which can be beneficial for use

---

* Corresponding author.
E-mail address: drparsu8@gmail.com (P.N. Sudha).

http://dx.doi.org/10.1016/j.ijbiomac.2017.01.142
0141-8130/

in air cleaning and water purification applications. The increasing need for new and low-cost adsorbents, ever growing problems of waste disposal, the high cost of synthetic resins and high ability and selectivity of chitosan for metal sorption, make it one of the most suitable materials for wastewater treatment [18].

Among the heavy metals, chromium is one of the most hazardous heavy metal, which is used widely by several industries, including dyes, electroplating, textile and alloying [19,20]. Chromium exists in two oxidation states Cr (VI) and Cr (III) [21]. The Cr (VI) state is 500 times more toxic to human health than the trivalent one [22]. Soluble Cr (VI) pollutes water, which would cause lung cancer [23]. Hence, it is necessary to remove Cr (VI) from wastewater to prevent the serious threat of Cr (VI) on ecosystem and public health. A large number of treatment methods in Cr (VI) removal have been reported, including adsorption [24,25], membrane separation [26,27], coagulation and precipitation [28,29], ion exchange [30,31] and solvent extraction [32]. Compared with other methods, adsorption process is generally recognized as the most promising and widely used feasible technique due to its low cost, high efficiency, regeneration and friendly to environment [33,34].

Copper serves as an essential co-factor for several oxidative stress-related enzymes including catalase, superoxide dismutase, peroxidase, cytochrome, oxidases, ferroxidases, monoamine oxidase, and dopamine β-monooxygenase [34–36]. Hence, it is an essential nutrient that is incorporated into a number of metalloenzymes involved in haemoglobin formation, carbohydrate metabolism, catecholamine biosynthesis, and cross-linking of collagen, elastin, and hair keratin. The ability of copper to cycle between an oxidized state, Cu(II), and reduced state, Cu(I), is used by cuproenzymes involved in redox reactions [34–36]. However, it is this property of copper that also makes it potentially toxic because the transitions between Cu(II) and Cu(I) can result in the generation of superoxide and hydroxyl radicals[34–37]. Also, excessive exposure to copper has been linked to cellular damage leading to Wilson disease in humans [36,37]. Hence it becomes important to remove excessive copper and chromium from water using low cost and highly efficient adsorbent.

The main objective of present study was to investigate the feasibility of a hybrid material, namely Chitosan-g-Maleic anhydride-g-(ethylene dimethacrylate) for the removal of Cu(II) ions from aqueous solution. The experimental data were fitted with the mathematical modelling such as Langmuir and Freundlich, isotherm models. The results were also analyzed on the basis of Lagergren pseudo-first order and pseudo-second order kinetics equation. Batch adsorption studies were conducted to evaluate the metal adsorption capacity of the Chitosan-g-Maleic anhydride-g-(ethylene dimethacrylate) copolymer.

2. Materials and methods

2.1. Materials

Chitosan (92.5% DD, 1000 kDa MW) was obtained from India sea foods Cochin, Kerala, India. The monomer maleic anhydride and ethylene dimethacrylate were of analytical grade and purchased from Merck, India. All other chemicals were of analytical grade and used as such.

2.2. Preparation of Chitosan-g-Maleic anhydride

Chitosan (2 g) and maleic anhydride (5 g) were dissolved in 100 mL of acetic acid and 10 mL of ceric ammonium nitrate (0.5 g) dissolved in10 ml of nitric is added. The mixture was stirred constantly at 70 °C for 3 h under nitrogen atmosphere. The resultant solution was cooled to room temperature and poured into 10% NaOH to precipitate the product. The product was filtered and washed with diethyl ether for several times and then dried in vacuum at 40 °C. The greyish white powder of Chitosan-g-Maleic anhydride was obtained.

2.3. Preparation of Chitosan-g-Maleic anhydride-g-ethylene dimethacrylate

The co-polymer was homogeneously synthesized in aqueous solution using ceric ammonium nitrate as the initiator. A mixture of 0.5 g Chitosan-g-Maleic anhydride was dissolved in 150 mL formic acid followed by the addition of ethylene dimethacrylate (2 g) dissolved in ethanol. The reaction was carried out at 70 °C for about 30 min. The contents of the flask were cooled to room temperature and poured into 10% NaOH solution to precipitate the graft co-polymer.

2.4. Characterization of CS-g-MA-g-EDMA

FTIR spectra of the samples as solid by diluting in KBr pellets were recorded with the Perkin Elmer Spectrum1 FTIR spectrometer at a resolution of 1 cm^{-1} at a scan range of 450–4000 cm^{-1}.

2.5. Batch adsorption studies

Batch adsorption method was used in this study. Synthetic solution of Cr(VI) and Cu(II) ion taken in stoppered bottles and agitated with composite films at 25 °C in orbit shaker at fixed speed, 160 rpm. The extent of heavy metal removal was investigated separately by changing adsorption dose, contact time of shaking and changing pH of the solution. After attaining the equilibrium adsorbent was separated by filtration using filter paper and aqueous phase concentration of metal was determined with atomic adsorption spectrophotometer (Varian AA 240).

3. Results and discussion

3.1. FTIR studies

FTIR spectrum of pure chitosan (spectrum not given) shows a broad peak around 3429 cm^{-1} due to —NH stretching and —OH stretching and the peaks around 1640 cm^{-1} and 1592 cm^{-1} due to amide I and amide II groups. The characteristic C—O stretching vibration appears at 1087 cm^{-1} and the C—N stretching vibration at 1485 cm^{-1}. The aliphatic (—CH_2) stretching vibration shows a peak at 2923 cm^{-1}. FTIR spectrum of Chitosan-g-Maleic anhydride is shown in (Fig. 1a). The strong band appears at 1596 cm^{-1} indicates C═C bond. This confirmed the grafting of malefic anhydride group onto chitosan.

Maleilated chitosan when grafted further with ethylene dimethacrylate Chitosan-g-Maleic anhydride-g-(ethylene dimethacrylate) copolymer was formed. The FTIR spectrum (Fig. 1b) had additional vibration bands at 1643 cm^{-1}, 1387 cm^{-1} due to carbonyl stretching. The symmetrical and asymmetrical peaks of the aliphatic groups (—CH_3, —CH_2) are obtained around 2898 cm^{-1} and 2826 cm^{-1}. The characteristic ester (—C—O—C—) vibration band appears at region 1267–1155 cm^{-1}. The FT-IR spectrum shows the characteristic peaks of chitosan, Chitosan-g-Maleic anhydride and Chitosan-g-Maleic anhydride-g-ethylene dimethacrylate copolymer. The peak shift to the higher wave number in the FTIR spectrum of double grafted copolymer confirmed grafting. It indicates the characteristic vibration peaks for (COO—, C═C, —C—O—C—, aliphatic appears and amide).