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Modified chitosan for the collection of reactive blue 4, arsenic and mercury from aqueous media

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ABSTRACT

In the present investigation a series of modified chitosan as adsorbents were synthesized free radically at 70 °C using acryloylated chitosan (AC-chitosan) as macromer, 2-acrylamido-2-methyl-1-propansulfonic acid (AMPS), 2-(diethylamino) ethylmethacrylate (DAEMA) as co-monomers and *N,N′*-methylene bisacrylamide (N-MBA) as a crosslinker for using as adsorbents in effluent remediation. Their structures (^{1}H and ^{13}C NMR), thermal stability (TG/DTG), surface morphology (SEM), reactive blue 4 (RB4), toxic metals such as arsenic (AsO^{2-}) and mercury (Hg^{2+}) uptake, swellability and reusability were evaluated. The adsorption of RB4 (701 mg/g), and the uptake of AsO^{2-} (551 mg/g) and Hg^{2+} (455 mg/g) showed Langmuir isotherm behavior with pseudo-first-order kinetics. The diffusion of water, RB4, AsO^{2-} and Hg^{2+} into the matrix followed non-Fickian mechanism. The evaluated changes in Gibbs free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) for adsorption indicated that the process was exothermic.

1. Introduction

Increased industrialization and urbanization globally have resulted in the enormous discharge of industrial effluents with colored pigments such as dyes from textile industries and toxic heavy metal ions such as arsenic (As^{3+}) from electronic, wood and leather tanning industries (Nami Kartal & Imamura, 2005), mercury (Hg^{2+}) from electro chemical, metal extraction and refining industries, etc. seriously polluting soil and water bodies. The typical concentration range of As^{3+} and Hg^{2+} metal ions reported for industrial effluents were 0.25 to 100 mg/L and 0.1 to 100 mg/L, respectively (Dinesh & Pittman, 2007Anoop Krishnan & Anirudhan, 2002). Such toxic metal ions and dyes beyond certain concentration limits in effluents can cause potential hazards such as skin, lung and kidney cancers and affect digestive system (Rajeswari, Namasivayam, & Kadirvelu, 2001) of mankind and harmful to other living beings if improperly handled. A very high exposure to inorganic arsenic can cause infertility, skin disturbances, declined resistance to infections, heart disruption, and DNA and brain damage (Musico, Santos, Dalida, & Rodrigues, 2013). Inorganic mercury poisoning is associated with psychological changes, spontaneous abortion and congenital malformation. In addition, the organic monomethylmercury causes damage to the brain and the central nervous system and reduction in root growth of aquatic plants. The unabsorbed dyes from the textile dying effluents are having low biochemical oxygen demand and high chemical oxygen demand values (Rajeswari et al., 2001). Besides, they are threatening the aquatic life, agricultural cultivation and underground water even at trace levels. Hence it is necessary to remove these toxic metal ions and dyes from the effluent to the tolerable level before being discharged into land and water using appropriate methods. Adsorption technique is the widely used cost effective method in the effluent treatment. Generally activated carbon, natural clays (Tahir & Rauf, 2006), modified clays (Baskaralingam, Pulikesi, Ramamurthi, & Sivanesan, 2006), fly ash (Dhodapkar, Rao, Pande, & Kaul, 2006) etc. are considered to be cost effective adsorbents to bring down the concentration of unabsorbed dyes and toxic metal ions from effluents.

In recent years hydrogels are increasingly being used as adsorbents to remove dyes, toxic metal ions and other pollutants from effluent (Paulino et al., 2006; Wang & Liu, 2013) which involves physico-chemical interaction of dyes and chelation of toxic metal ions. Hydrogels, a class of physico-chemically crosslinked three-dimensional network hydrophilic polymers can imbibe and retain considerable amount of water and water soluble substances without dissolving and losing their structural integrity. Due to these properties, they are finding widespread applications (Guilherme et al., 2005) in bioengineering, biomedicine, agriculture, food

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industry, water purification, separation process, effluent treatment etc. It has been reported (Bayramoglu, Yakup Arica, & Bektas, 2007) that the adsorption capacity of hydrogel can be improved by introducing some natural preformed polymer such as alginates (Dhanapal & Subramanian, 2014), chitosan, etc. during hydrogel synthesis or by growing hydrophilic moiety on chitosan/alginates by graft copolymerization of appropriate hydrophilic monomers. Among the polysaccharides, chitosan, chitosan derivatives or chitosan modified by methods such as radical grafting of monomers, reinforcing with clay, blending with other polymers, IPN formation, etc. were widely used as adsorbent materials for the removal of dyes and toxic metal ions from effluents through adsorption or chelation mechanism (Liu, Wang, Yu, & Meng, 2013; Wan Ngah, Teong, & Hanafiah, 2011; Crini & Badot, 2008; Bayramoglu et al., 2007). Chelation is the prevalent mechanism of collection of transition and post-transition metal ions by chitosan amino groups (Muzzarelli & Rocchetti, 1974; Muzzarelli, 1977; Muzzarelli, 2011). Incorporation of highly hydrophilic hydrogel segments on chitosan may improve the collection of metal ions and dyes from aqueous medium through adsorption (Paulino et al., 2006; Wang & Liu 2013). Hence, the present investigation involves linking of hydrophilic segments by copolymerizing the monomers AMPS and DAEMA in presence of a crosslinker N-MBA via the *N*-acryloly group of chitosan by appropriate synthetic strategy to enhance the adsorption or chelation capacity of modified chitosan.

2. Experimental

2.1. Materials

AMPS, N-MBA (Aldrich) were purchased and used as received. DAEMA (Aldrich) and acrylic acid (AA, Himedia, Mumbai) were purified by column chromatography. Potassium persulphate (KPS, NICE, Cochin) and chitosan were used after recrystallization in distilled water and re-precipitation, respectively. Hydrochloric acid (HCl), potassium iodide (KI), RB4, rhodamine-B (RhB) (Himedia, Mumbai), benzoyl chloride (BC), hydroquinone (HQ), *N*,*N*′-dimethy formamide (DMF), dimethyl sulfoxide (DMSO), poly(vinyl alcohol) (PVA), mercury(II) chloride, sodium arsenite (Merck), acetone, methanol, sodium hydroxide (NaOH), acetic acid (Rankem, New Delhi) were of analytical grade and used as received.

2.2. Synthesis of acryloyl chloride (ACOCl)

ACOCl was synthesized by reflexing AA (0.8 mol), BC (2.66 mol) and HQ (2 g, polymerization inhibitor) in a 500 mL round bottom flask at 80°C for 2 h in nitrogen atmosphere and collecting the fraction distilled at 90°C (Siva Bharathi, Mohan Reddy, Ramachandra Reddy, & Venkata Naidu, 2010). The liberated HCl was trapped in 0.1 N NaOH solution. The collected impure ACOCl was redistilled at 72°C and the fraction (yield 65%) collected was used in subsequent experiment.

2.3. Synthesis of AC-chitosan

A chitosan solution prepared by dissolving ten grams of purified chitosan powder in 50 mL of 1% acetic acid solution taken in a 250 mL round bottom flask was charged with 75 mL DMSO and the mixture was heated to 100°C to facilitate complete dissolution of chitosan. To this 20 mL of DMF and 1.5 mL of pyridine were added under continuous stirring over a period of 5 min and then cooled to 0°C. In sequence, 3 mL of ACOCl in 5 mL DMF were drop wise added to this solution with constant stirring and left aside for 2 h at 0°C (Jayakumar, Prabaharan, Reis, & Mano, 2005; Pourjavadi, Jahromi, Seidi, & Salimi, 2010). The AC-chitosan thus formed was precipitated in acetone and repeatedly washed with acetone, air dried and stored for further use.

2.4. Synthesis of ACAD

Twenty two samples of ACADs as adsorbent materials with different compositions designated by ACAD-0, ACAD-1, ACAD-2... ACAD-20 and ACAD-21 were synthesized by radical copolymerization by taking various amounts of AC-chitosan, AMPS and DAEMA using N-MBA as a crosslinker and KPS as thermal initiator in a 50 mL stoppered borosilicate tube, at 70°C after nitrogen purging. Thus obtained ACADs were recovered by adding ice cold methanol and washed repeatedly with methanol. Then the crosslinked gels were cut into small pieces and dried to constant weight at 50°C in an air oven. Further, these ACADs were powdered and purified by Soxhlet extraction using acetone–methanol (1:1 v/v), at 70°C for 48 h. The purified ACADs were powdered, sieved and stored after vacuum drying.

2.5. Characterization techniques

The NMR spectra were recorded on Bruker Avance III 500 MHz multi nuclei NMR spectrometer at 500 MHz for ^{1}H and 125 MHz for ^{13}C (proton decoupled) in CD_3COOD/D_2O mixed solvents taking solvent peak as reference. TG/DTG studies were performed on TGA Q 500 V20.10 Build 36 with a sample size of 1.5–3.5 mg under air at a heating rate of 10 °C/min for the temperatures range from ambient to 800°C. The concentrations of dye and those of AsO^{2-} and Hg^{2+} metal ions were estimated spectrophotometrically on Perkin Elmer Lambda 35 UV–vis absorption spectrometer at 575 nm for dye and at 554 and 592 nm for metal ions complex with Rh B. SEM micrographs of equilibrium swelled, lyophilized ACAD and AsO^{2-} adsorbed ACAD at different magnifications were recorded on ZEISS EVO series SEM model EVO 50 microscope.

2.6. Water uptake measurements

The degree of water uptake of ACADs were measured using tea bag method (Dhanapal, Vijayakumar, & Subramanian, 2013) by taking 0.1 g of sieved ACAD sample in 200 mL of deionized water at 30°C under equilibrium swelling conditions (6 h). The swelling profiles ACADs were constructed by plotting the water uptake vs. time at 30°C. An average of three measurements were taken to calculate equilibrium swelling (ES) using the following equation:

$$ES = \frac{W_s - W_d}{W_d} \quad (1)$$

where W_s and W_d are the weights of the swollen and the dry polymer samples, respectively.

2.7. Column mode adsorption of metal ions and dye

Separate stock solutions of AsO^{2-} and Hg^{2+} were prepared by dissolving 1.733 and 1.350 g of sodium arsenite and mercury(II) chloride, respectively in 1000 mL deionized water. A series of RB4 solution of different concentrations (1, 2, 3, 4 and 5×10^3 mg/L) were prepared. The adsorption studies of AsO^{2-}, Hg^{2+} and dye from their respective solutions were performed on all ACAD samples at different swelling time, temperature and pH. The adsorption experiments were done using separate identical glass columns of 2 cm diameter and 86 cm length. The columns were filled with 10 g of powdered and sieved adsorbents (ACADs) without voids. Then, the synthetic effluent prepared using metal ion/or dye were eluted through these columns at a constant flow rate (2 mL/min) at 30°C. The effluent solutions were collected at different time intervals and the concentration of metal ions and dye in the collected