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A hybrid material for sustainable environmental protection

Anjali Bajpai[a*], Neha Tripathi[a]

[a] Department of Chemistry, Government Model Science College, Jabalpur 482001, India

Abstract

The hybrid nanocomposite was prepared by *in situ* intercalative polymerization of acrylamide in a fine dispersion of the sugarcane bagasse, chitin and fuller's earth by microwave irradiation. The product was very efficient as an adsorbent for metal ions and organic dye. It was mechanically stable in wet condition, resistant to fast microbial attack and released no leachates.

Keywords: hybrid nanocomposite; adsorbent; sugarcane bagasse; fuller's earth; chitin

1. Introduction

The 20th century witnessed the great industrial revolution which has changed the lifestyle of people on mother earth. The task for the present generation is to continue with the progress as well as to develop processes for sustainable environmental protection. Human activities, viz., domestic, industrial and agricultural, introduce a variety of pollutants in the natural water bodies, which are hazardous to living beings. Hence, the environmental protection authorities have imposed stringent regulations for treatment of effluents before their disposal into the water sources. Naturally there is an urgent demand for economic materials and convenient processes. A multitude of processes employed are: coagulation, precipitation, extraction, evaporation, adsorption on activated carbon, ion- exchange, oxidation, incineration, electro-floatation, electrochemical treatment, biodegradation and membrane filtration [1]. Adsorption is the most popular and widely used method. Activated carbon is the most significant adsorbent because it has a high capacity for adsorption of organic matter, but its use is limited due its high cost. This has led to search for economic substitutes [2-4].

The extreme variability of industrial wastewater must be taken into account in the design of any adsorbent system [5]. Polysaccharides are especially attractive as adsorbents because they are economical, abundant and biodegradable renewable resources. However, each type of pollutant may need a particular polysaccharide. Each polysaccharide has its specific application as well as inherent advantages and disadvantages in wastewater treatment. The ability of cellulose to adsorb organic dyes, metal ions is quite established but it is very low in comparison to activated carbon or zeolite. Further, the adsorption properties of native cellulose vary according to its origin and preliminary treatment [6]. The second abundant biopolymer in nature after cellulose is chitin, which is the most abundant natural amino polysaccharide. Chitin (CH) is insoluble and intractable; hence it is generally deacetylated to chitosan for various applications [7]. However, the use of chitosan to form superabsorbent materials has been limited because of their usually poor mechanical properties when compared to other polymers. The addition of reinforcing fillers into the hydrogel matrix can enhance their mechanical properties and improve their handling [8]. Fuller's earth (FE) is a fine-grained naturally occurring earth substance that has a substantial ability to adsorb impurities or coloring bodies [8]. Montmorillonite is the principal clay mineral in fuller's earth, but other minerals such as kaolinite, attapulgite and palygorskite also occur and account for its variable chemical composition.

* Corresponding author. Tel.: +91 0761 2601496; fax: +91 0761 2621272
E-mail address: abs_112@rediffmail.com

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A novel hybrid material was developed from economical, abundant renewable resources, *viz*. sugarcane bagasse (SCB), CH and FE. SCB, an agricultural waste and CH, a food industry waste have been reported to possess affinity for metal ions, dyes and other organic materials. Montmorillonite, the major component of FE owes great adsorption properties due to the presence of cations in interlayers. However, biomaterials suffer from the drawback of fast microbial degradation under wet environment and FE, the inorganic material swells and disperses in water, which renders separation cumbersome. Polyacrylamide is being popularly used as a polymeric flocculent but with the disadvantage of releasing oligomers in water, which is objectionable. It was envisaged that if a filter/adsorbent medium composed of an economic nanocomposite constituted from SCB, CH and FE could be developed, it would adsorb a variety of pollutants. A semi-interpenetrating network formed by polymerization of vinyl monomer would result in an organic-inorganic hybrid nanocomposite.

2. Materials and methodology

Locally available SCB was thoroughly rinsed with water to remove water soluble extractives, dried in an air oven at 60 °C for 72 h, finely ground, sieved and dispersed in 0.25 M aqueous sodium hydroxide solution and magnetically stirred for 48 h. CH flakes were dispersed in 20 % (V/V) acetic acid solution and magnetically stirred for 24 h. The resulting emulsions of SCB and CH were thoroughly mixed with finely powdered FE and acrylamide (AAm). Potassium persulphate (KPS) and N, N'-methylenebisacrylamide (MBA) were added and the mixture was again stirred magnetically, and then finally irradiated in a domestic Kenstar microwave oven. The product was thoroughly extracted with water to eliminate loosely bound material. The compact mass was then dried in an air oven. Swelling properties were studied using conventional gravimetric procedure [10]. Accurately weighed pieces of the sample (mass m_o) were immersed in 200 mL of deionized water for 24 h in respective experiments. The swollen samples were taken out, dried in an air oven and weighed again (mass m_d). Percent erosion was calculated using the equation 1.

$$\% \quad Erosion = \frac{m_0 - m_d}{m_0} \times 100 \tag{1}$$

Dye loading was accomplished by placing the 1 g samples of nanocomposite in 200 mL of various concentration of methyl orange aqueous solution at room temperature for overnight. The samples were removed from the bath and washed with deionized water to remove excess of dye adhered at the surface of sample and dried at room temperature. Concentration of the dye solutions were determined by a UV-visible spectrophotometer. For the study of metal ion adsorption Nanocomposite samples were dipped in 0.1 M acidified aqueous solutions of Cu^{2+} or Ni^{2+}, Hg^{2+} at room temperature for 24 h then 1 mL of aliquot was pipetted out and diluted with deionized water till desired concentration. The concentrations of metal ions in respective solutions were measured with a Shimadzu 6300 atomic absorption spectrometer. Percent adsorption was determined by following equation.

$$\% \text{ Adsorption} = (C_0 - C / C_0) \times 100 \tag{2}$$

Where, C_0 and C (g/L) are the concentrations of adsorbate in the solution before and after the adsorption, respectively.

3. Results and discussion

A multicomponent nanocomposite was prepared by intercalative polymerization of AAm in presence of sugarcane bagasse, chitin and fuller's earth. In the present study methyl orange was used as a model organic dye; and nickel, copper, and mercury as representative metal ions for evaluation of efficiency of this material as an adsorbent. SCB is the fibrous residue obtained from sugarcane juice extraction and consists of cellulose (50 %), hemicelluloses (25 %) and lignin (25 %) as the principal constituents [11]. SCB fibres were treated with 0.25 M NaOH solution to dissolve hemicellulose and lignin, and the suspension obtained was used as such for preparing the nanocomposite. Shaikh et al. [12] reported utilization of the hemicellulose as internal plasticizer. Similarly lignin would provide additional binding to the various constituents of nanocomposite and would impart slight hydrophobicity needed for mechanical stability under water swollen condition. Inclusion of lignin in printing inks and paint vehicles, showed a drastic reduction in misting, without any accompanying detrimental effects to their other functional parameters [13]. A reinforcement effect was reported on incorporation of lignin into composites [14,15]. Chitin a β –(1, 4)–linked polymer of 2-acetamido-2-deoxy-D-glucopyranose (N-acetyl-D-glucosamine) was pre-treated with 20% acetic acid to disperse it homogeneously in the reaction mixture as far as possible. It has been shown that amorphous regions in cellulose, chitin and chitosan are susceptible to acid attack allowing the formation of nanofibrils [16-18]. These nanofibrils show excellent dispersion in water [19,20]. Further their good dispersion in the polymeric matrix nanofibrils is possible through interactions among the nanosized moieties that form a percolated network connected by hydrogen bonds [21,22]. In the present study dilute solution of a week acid (acetic acid) was employed so that a partial dispersion of material could occur and the remaining aggregates would act as the reinforcing fillers.