International Journal of Biological Macromolecules 86 (2016) 750–755

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Remediation of distilleries wastewater using chitosan immobilized Bentonite and Bentonite based organoclays

F.I. El-Dib, F.M. Tawfik, Gh. Eshaq, H.H.H. Hefni, A.E. ElMetwally *

Department of Petrochemicals, Egyptian Petroleum Research Institute, Nasr City, Cairo 11727, Egypt

ARTICLE INFO

Article history:
Received 19 December 2015
Received in revised form 26 January 2016
Accepted 28 January 2016
Available online 1 February 2016

Keywords:
Catalysis
Adsorption
Bentonite
Chitosan
Wastewater treatment

ABSTRACT

Organic–inorganic nanocomposite, namely chitosan immobilized Bentonite (CIB) with chitosan content of 5% was synthesized in an acetic acid solution (2%). Organically modified CIB and Bentonite (mbent.) were prepared by intercalating cetyl trimethylammonium bromide (CTAB) as a cationic surfactant at doses equivalent to 1.5 and 3 times the cation exchange capacity (CEC) of clay. The prepared samples were characterized using FTIR, XRD and SEM to explore the interlayer structure and morphology of the resultant nanocomposites. The remediation of distilleries (vinasse) wastewater process was carried out using different adsorbents including CIB, modified CIB (mCIB), Bentonite (bent.), modified Bentonite (mbent.) and chitosan at different contact time. The results showed that the packing density of surfactant used in the synthesis of organoclays strongly affects the sorption capacity of the clay mineral and also showed that $(mCIB)_3$ was found to be the most effective sorbent in the purification of distilleries wastewater with 83% chemical oxygen demand (COD) reduction and 78% color removal.

1. Introduction

Molasses spent wash is the waste product produced after the distillation of ethyl alcohol from molasses, a typical of that type of liquid waste is called vinasse. This waste is highly hazardous to the environment due to its high acidic nature (pH 4–4.3) and high chemical oxygen demand load. According to previous studies, about 8–15 l molasses spent wash is generated during the production of 1 l of ethanol. Effluent from distilleries contains a large amount of dissolved organic and inorganic matter. Distillery spent wash is not only high on organic and inorganic loading, but also has dark brown color even after industrial standard treatment using anaerobic digestion/bio-methanation. Effective treatment of organic and inorganic pollutant in industrial discharge has been a major challenge for us. This organic matter is readily decomposed by biological action; consequently, its discharge to the water surface causes serious damage to aquatic life in the stream. Spent wash also leads to significant levels of soil pollution and acidification because of low pH of wastewaters in the case of inappropriate land disposal. It is also reported to inhibit seed germination, reduce soil alkalinity and manganese availability and damage agricultural crops [1,2]. The process of removal of toxic chemicals is definitely a challenging task before environmental scientist and engineers. Various naturally occurring substances like clay, sand coal and stone are used as a softener of wastewater [3,4].

Clay minerals are the most important inorganic component in soil due to their excellent mechanical and chemical properties and consequently they are widely used in environmental application [5]. The hydration of inorganic cations on the exchange sites causes the clay mineral surface to be hydrophilic, therefore the natural montmorillonite is an ineffective sorbent for organic compounds [6]. However, such a difficulty can be overcome by intercalating cationic surfactant such as quaternary ammonium salts into the interlayer space by ion exchange [7]. The intercalation of cationic surfactant not only changes the surface properties from hydrophilic to hydrophobic but also increases the basal spacing of the layers [8].

Chitosan is a modified, natural carbohydrate polymer derived from the chitin component of crustacean exoskeleton such as shrimp, crab, crawfish etc. Chitosan is well known to be an excellent adsorbent because it contains hydroxyl (—OH) and amino ($-NH_2$) groups that serve as metal binding sites [9]. However, chitosan has a low surface area, with weak chemical and mechanical properties. Consequently, the modification of these physical and chemical properties is essential to overcome these obstacles. These modifications facilitate the enlargement of chitosan chain, which in turn reduce its crystallinity and make the biding sites more accessible [10].

* Corresponding author. Fax: +20 2 22747433.
E-mail addresses: ahmed_ezzatt@msn.com, aezzat24@gmail.com (A.E. ElMetwally).

http://dx.doi.org/10.1016/j.ijbiomac.2016.01.108
0141-8130/

Table 1
Characteristics of the vinasse.

pH	4.76
COD mg/l	10,1791
Total solids (%w/w)	8.7
Organic acid (as acetic acid) (%w/w)	0.24
Color	Dark brown and disagreeable smell

In the present study, chemical modification of chitosan has been carried out through immobilization of chitosan on Bentonite. Next, CIB was modified by intercalating CTAB into the interlayer space of Bentonite and the product is denoted as (mCIB). The main objectives of this study were to utilize low cost and naturally occurring adsorbents in treatment of wastewater from distilleries according to the following steps:

1. Preparation of modified chitosan immobilized Bentonite (mCIB) and modified Bentonite (mbent.) using cationic surfactant (CTAB).
2. The resultants (mCIB) and (mbent.) were characterized using FTIR, XRD and SEM techniques to explore the interlayer structure and morphology of the resultant composites.
3. Comparing the efficiency of treated and untreated Bentonites for the removal of color and reduction of COD from distillery spent wash (vinasse).

2. Experimental

2.1. Materials and equipments

Chitosan flakes with 82% degree of deacetylation and 110 kDa of molecular weight was prepared according to the method in the literature [11]. Bentonite from El-Tih region (East Abu-Zenima, Sinai Peninsula, Egypt) was ground, sieved to particle diameter less than 125 μm, and then subjected to activation by treatment via 2% hydrochloric acid solution for 6 h at 104 °C in order to remove carbonates and soluble salts [12]. The clay was washed repeatedly with distilled water then dried at 120 °C for 2 h. The cation exchange capacity (CEC) of the resultant Bentonite was found to be 80 meq/100 g of clay. Trimethylammonium bromide (CTAB) with an average molecular weight of 364.45 g mol^{-1} was purchased from Loba Chemie (India). Vinasse was supplied by the Egyptian Hawamdya sugar company and its characterizations are presented in Table 1. To imitate the real wastewater, tenfold diluted vinasse was used in our experiments. XRD analysis was performed using a Bruker D8 series with a slow scan at 0.3 S^{-1} in 2θ range of 4–70°. FTIR measurements were performed using a Nicolet IS-10 FTIR instrument with KBr discs. Chemical oxygen demand (COD) was determined according to ASTDM 1252 using standard HACH COD vials. The degree of color elimination was determined spectrophotometrically at 455 nm.

2.2. Preparation of chitosan-immobilized Bentonite

A 5.0 g of chitosan was dissolved in 300 ml of 5% (vol/vol) HCl under vigorous stirring for 2 h. After chitosan dissolution, 100 g of clay (Bentonite) was added to the solution and stirred for 3 h at 25 °C. The pH of the resultant slurry was then neutralized using NaOH (1 M) to immobilize chitosan on Bentonite as described in our previous study [13]. The chitosan-Bentonite beads were filtered and washed with deionized water to remove the excess NaOH. The obtained CIB was dried in the oven at 65 °C for 24 h. The dried sample was grinded and sieved using ASTM sieve size no. 35 and no. 45 to obtain CIB beads with a size range of 0.35–0.50 mm.

2.3. Preparation of modified Bentonite (mbent.) and modified chitosan immobilized Bentonite (mCIB)

The organoclays were prepared by adding certain amount of CTAB equivalent to 1.5 and 3CEC of the clay to ensure complete exchange of inorganic cations. CTAB solution was prepared by dissolving an appropriate amount of CTAB in deionized water. Next, CIB or pristine Bentonite was dispersed in CTAB solution under mechanical stirring for 48 h. The resultant organoclays were then separated via filtration, washed twice with deionized water, dried at 70 °C and eventually stored for further use in the adsorption tests. The prepared samples were denoted as $(mCIB)_3$, $(mbent.)_{1.5}$, $(mbent.)_3$, where 1.5 and 3 refer to the amount of CTAB equivalent to 1.5 and 3 CEC of the clay.

2.4. Adsorption studies

In the present study, diverse adsorbents including pristine Bentonite, pristine chitosan, $(mbent.)_{1.5}$, $(mbent.)_3$, and $(mCIB)_3$ were tested in the color removal and COD reduction of distilleries wastewater. Model experiments with tenfold diluted vinasse were carried out to determine the adsorption capacity of different adsorbents with concentration of 15 g l^{-1}. Appropriate amounts of adsorbents were added to vinasse solution (50 ml) under continuous stirring at 25 °C for 3 h. The kinetics of organic acid adsorption on the surface of adsorbents was studied by measuring the change in pH value of the mixture at definite time intervals. When the adsorption experiments were complete, the adsorbents were immediately separated by filtration and the filtrate was analyzed for color determination and COD reduction.

3. Results and discussion

Chemical modifications afford novel types of hybrid materials composed of natural polysaccharides and low cost inorganic materials (clays). Surfactant modification of the above synthetic, organic–inorganic composites can introduce the desired properties and enlarge the field of their potential applications as adsorbents for wastewater treatment. Herein, surfactant was used to intercalate either virgin Bentonite or CIB composite to improve their performance as adsorbents in the treatment of distilleries (vinasse) wastewater.

3.1. Characterization of modified chitosan immobilized Bentonite and modified Bentonite

3.1.1. FTIR

As mentioned in our previous publication, Fig. 1 compares the FTIR spectra of CIB, Chitosan and Bentonite [13]. A sharp intense band at 3697 and 3622 cm^{-1} assigned to —OH stretching vibrations of Bentonite and attributed to the inner hydroxyl units within the clay layers. The appearance of this sharp band in CIB composite with the same intensity and position indicates that chitosan was not intercalated within the silicate layer [14,15]. At the same time, the band appears at 3429 cm^{-1}, which corresponds to the hydroxyl group on clay surface in pristine Bentonite, is shifted to lower frequency (3418 cm^{-1}) upon the immobilization of chitosan, suggesting an interfacial interaction between chitosan and Bentonite surface (Scheme 1A) [16]. The additional band appears at 1475 cm^{-1} in modified clays (Fig. 2a–c) corresponds to C—N vibration in tertiary amine, which is absent in the untreated Bentonite and CIB (Fig. 1b and c). FTIR spectrum of CTAB shows absorption bands at 2849 and 2918 cm^{-1} (Fig. 2d), correspond to the symmetric and asymmetric stretching vibrations of C—C in the alkyl chain [17]. On the other hand, the FTIR spectrum of modified clay (Fig. 2a) shows bands appear at 2924 and 2852 cm^{-1}, which correspond to