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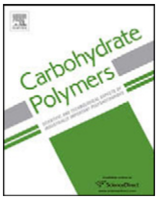

Radiation synthesis, characterization and dye adsorption of alginate–organophilic montmorillonite nanocomposite

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ABSTRACT

In this paper, the preparation, characterization and dye adsorption properties of nanocomposite (calcium alginate/organophilic montmorillonite) (CA/OMMT) were investigated. A new nanocomposite consisting of alginate and OMMT was prepared by polymerization using γ-rays irradiation as initiator. Physical characteristics of CA/OMMT were studied using X-ray diffraction (XRD), infrared spectrophotometery (IR), thermal gravimetric analysis (TGA), transmission electron microscopy (TEM) and the corresponding selected area electron diffraction (SAED). Two textile dyes, acid green B and direct pink 3B, were used as model anionic dye. Factors affecting dye sorption, such as pH, sorbent concentration and temperature of each dye solution were extensively investigated. It was found from the study that the sorption of dyes by the nanocomposite is pH-dependent and maximum sorption was obtained at pH 2. The thermodynamic data showed that dye adsorption onto alginate was spontaneous, exothermic, and a physisorption reaction. On the basis of the data of the present investigation, one could conclude that the as-prepared adsorbents exhibited excellent affinity for the dye, and can be applied to treat wastewater containing anionic dyes.

1. Introduction

Dyes have been the subject of many interests in recent years because of increasingly stringent restrictions on the organic content of industrial effluents (Abou Taleb, Abd El-Mohdy, & Abd El-Rehim, 2009). Dyes are one of the most hazardous chemical compound classes found in industrial effluents and need to be treated since their presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora (Royer et al., 2009). They are also aesthetically objectionable for drinking and other purposes (Royer, Cardoso, Lima, Macedo, & Airoldi, 2010). Dyes can cause allergy, dermatitis, skin irritation (Brookstein, 2009) and also provoke cancer and mutation in humans (Carneiro, Umbuzeiro, Oliveira, & Zanoni, 2010).

The most efficient method for the removal of synthetic dyes from aqueous effluents is the adsorption procedure (Olivares-Marín et al., 2009; Calvete, Lima, Cardoso, Dias, & Pavan, 2009). This process transfers the dyes from the water effluent to a solid phase, thereby keeping the effluent volume to a minimum (Cuerda-Correa, Domínguez-Vargas, Olivares-Marín, & de Heredia, 2010; Malarvizhi & Ho, 2010). Subsequently, the adsorbent can be regenerated or stored in a dry place without direct contact with the environment (Calvete et al., 2010a; Calvete, Lima, Cardoso, Dias, & Ribeiro, 2010b). From the view of industrial application, removal of dyes by adsorption is a promising approach because of its low performance cost and easy technical access (Kumar, Ramamurthi, & Sivanesan, 2005). In addition, the adsorption processes give the best results as they can be used to remove different types and concentrations of dyes, providing an attractive treatment, especially if low-cost adsorbents are used. Many adsorbents have been employed to remove dyes from effluents.

Very recently, the application of hydrogels as adsorbents has been paid special attention. Hydrogels with three dimensional crosslinked polymeric structures and hydrophilic groups can swell considerably in aqueous solution without dissolution because hydrophilic chains contact one to the other by cross-links (Sannino et al., 2005). Hydrogels have many predominant properties including low interfacial tension and a variety of functional groups which can trap ionic dyes from wastewater and endowed hydrogels with high adsorption capacities, which is a favor for the treatment of the environment (Yi & Zhang, 2008). But pure hydrogels often have some limitations such as low mechanical stability and gel strength and introduction of clays materials into hydrogels can overcome these drawbacks because hydrogels with clays materials combine elasticity and permeability of the gels with high ability of the clays to adsorb different substances (O¨ztop, Hepokur, & Saraydin, 2010). As a consequence, much research concerning hydrogels with clays

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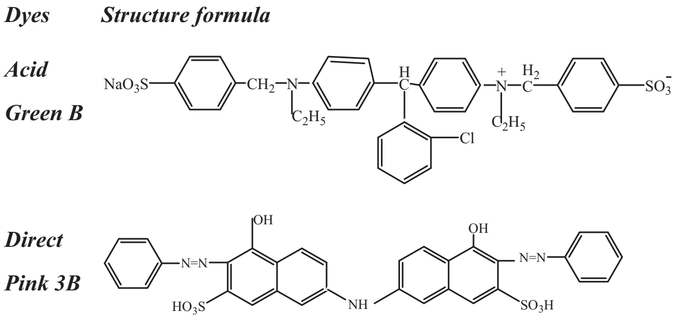

Chart 1. Chemical structure of dyes.

materials adsorbing dyes (Kaşgöz & Durmus, 2008) and metal ions (Chen & Wang, 2009) have exponentially increased.

The organoclay is a very important application of clay minerals and has been widely used as adsorbents of organic pollutants in soil, water and air. An interesting phenomenon has been observed that organic modification can significantly improve the clay's adsorption capability toward anionic dyes. However, investigations on the adsorption mechanism of this process are relatively scarce. At present, the main mechanism proposed is believed to be the binding between anionic groups (e.g., sulfonic groups) of the dye and the positively charged surface of organoclays (Zhu & Ma, 2008; Pulikesi, Ramamurthi, & Sivanesan, 2006). Recent research about the adsorption of anionic dyes on organoclays rarely deals with the effect of the loading of organic cations on the dye's removal.

Alginate is a naturally occurring carbohydrate polymer and has a capacity to remove toxic pollutants. One of the important properties of alginate is the ability to form hydrogels (Jankowski, Zielinska, & Wysakowska, 1997). An aqueous solution of alginate is readily transformed into a hydrogel on addition of metallic divalent cations such as Ca^{2+}. Calcium alginate immobilized microbial cultures have been used for decoloration of dyes (Aravindhan, Fathima, Rao, & Nair, 2007; Ramsay, Mok, Luu, & Savage, 2005). The aim of this study is to focus a synthesized CA/OMMT nanocomposites initiated by γ-ray irradiation polymerization. The objectives of this study are to investigate the effects of the prepared nanocomposite on the structural, thermal, and the retention of anionic dye pollutants such as acid green B and direct pink 3B dyes using CA/OMMT nanocomposites.

2. Materials and methods

2.1. Chemicals

Sodium alginate (SA) and triethyl amine used in this study were a laboratory grade chemicals obtained from Aldrich Chemical Co. (Milwaukee, WI, USA) and used as received. The clay mineral used in this study was sodium montmorillonite. Two different types of dyes were used as adsorbents. The dyes used in the experiments were acid green B (λ_{max} = 636 nm) and direct pink 3B (λ_{max} = 526 nm). Dyestuffs and Chemicals Co., Kaffer El-Dawar, Egypt supplied all of these dyes. The chemical structures of different dyes are depicted in Chart 1. All of the dyes were commercial grade and were used without any further purification. The other chemicals and phosphate buffers were reagent grade and used as received. In addition, distilled water was used as a solvent. Structures of the dyes are shown.

2.2. Preparation of reactive intercalating agents for clay

Vinyl benzyl triethyl ammonium chloride (VBTAC) was prepared according to Mulvancy and Chang (1977).

2.3. Modification of clay (OMMT)

The cation exchange procedure was followed using previously described methods (Al-Sigeny, Abou Taleb, & El-Kelesh, 2009).

2.4. Synthesis of CA/OMMT nanocomposites

An exact amount of alginate (SA) was first dissolved in distilled water to prepare 3 wt% solutions. The nano particle loadings were varied as 0%, 1%, 3% and 5% OMMT of the combined weight of the SA. After constant stirring for 30 min, the system was deoxygenated by degassed for 10 min. Irradiation to the required doses (20 kGy) was carried out in a ^{60}Co gamma cell (made in Russia) facility of the National Center for Radiation Research and Technology, Cairo, Egypt at a dose rate of 2.86 Gy/s. $CaCl_2$ (3 wt%) was used in the final feeding solutions of hydrogels, after gamma irradiation, to form network structure of calcium alginate (CA). After completion of the reaction, the contents were cooled and cast on a glass plate, the solvent was then evaporated and sample films were obtained.

2.5. Instrumentation

The XRD analysis was performed using XD-DI Series, Shimadzu apparatus using nickel-filtered and Cu-Kα target.

FTIR spectra were recorded on Mattson 1000, Unicam infrared spectrophotometer Cambridge, England in the range from 400 to 4000 cm^{-1} using KBr pellets.

Thermogravimetric analyzer Shimadzu TGA system of Type TGA-50 was used in this study. The temperature range was from ambient to 600 °C at heating rate of 10 °C/min in nitrogen atmosphere 20 mL/min.

The surface morphology of the copolymer was examined with a Jeol JSM-5400 scanning electron microscopy (SEM) (JEOL, Tokyo, Japan).

TEM measurements: The as-prepared powders were suspended in ethanol and a drop of the resultant mixture was deposited on an ultra thin carbon supported Cu grid, and air-dried. Energy-filtered electron powder diffraction used TEM JEOL: JEM-100cx.

Absorbance measurement was carried out on UNICAM UV–Vis Spectrometer. 1000 Model spectrophotometer.

2.6. Water uptake measurements

The clean, dried sample nanocomposites of known weights were immersed in distilled water at 25 °C until equilibrium was reached (almost 24 h). The samples were removed, blotted quickly with absorbent paper and then weighed. The uptake percentage of these samples was calculated using the equation:

$$\text{Water uptake\%} = \frac{w_s - w_d}{w_d} \times 100$$

where w_d and w_s represent the weights of dry and wet sample nanocomposites, respectively.

2.7. Adsorption studies

Adsorption isotherms were determined by the batch method for all adsorbents. Accurately weighted dry samples (0.1 g) were placed in a solution of a definite volume (25 mL) and allowed to stand for a period of 4 days at room temperature. Adsorption amount of dye (mg/g) was calculated by using the following equation:

$$q_e = \frac{[(C_0 - C_e) \times V]}{W}$$

where W is the weight of dry (CA/OMMT) nanocomposites (g); V is the volume of the aqueous phase (L); q_e is the amount of dye