Research paper

Sodium montmorillonite/ureasil-poly(oxyethylene) nanocomposite as potential adsorbent of cationic dye

Yanisleidys Hernández Bermúdez*, Laurianne Truffault, Sandra Helena Pulcinelli, Celso Valentim Santilli

Universidade Estadual Paulista "Júlio de Mesquita Filho", Istituto de Química, Rua Prof. Francisco Degni 55, 14800-900, São Paulo, Araraquara, Brazil

ARTICLE INFO

ABSTRACT

A sodium montmorillonite/ureasil-poly(oxyethylene) clay-polymer nanocomposite was prepared using the sol-gel reaction of a U-PEO hybrid precursor/clay mineral suspension, with the aim of developing a sorbent for the removal of cationic dyes from aqueous media. The structural characteristics of the nanocomposite were studied by FTIR, XRD, UV–Vis spectroscopy, and SAXS. The XRD results revealed intercalation of the U-PEO in the silicate interlayer spaces. FTIR spectra indicated the existence of strong interactions between methylene blue (MB) dye and the clay mineral silicate layers. Time-resolved SAXS measurements during MB adsorption showed a decrease of the montmorillonite (Mt) peak area and an increase of the half-height width of the peak, indicating that water uptake during dye adsorption caused a reduction of the Mt. crystallite size. UV–Vis adsorption experiments showed that the kinetics of MB adsorption followed a pseudo-first order process and that the steady state equilibrium adsorption capacity followed the Langmuir model. The results showed that the nanocomposite is potentially applicable as an adsorbent of dyes present in contaminated waters.

1. Introduction

The development of science and technology has provided clear benefits to society, but at the same time has led to many environmental problems, such as contamination by effluents, air pollution, and climate change, among others. In addition to the fact that the availability of fresh water is decreasing due to high consumption by agriculture (70%), industry (22%), and households (8%) (Bhatnagar and Sillanpää, 2010), the wastewater that returns to the environment contains various contaminants, such as heavy metals or dyes, which are often difficult to biodegrade and are toxic to animals and humans (Aguiar et al., 2017). Different physical, chemical, electrochemical, and biological methods can be used to treat and reuse wastewater (Crini, 2006; Hajjaji et al., 2016). Among the physical-chemical methods, adsorption processes are of particular interest due to their speed, nontoxicity, relatively low cost, and efficiency in the removal of pollutants and treatment of large volumes of liquids (Allègre et al., 2006; dos Santos et al., 2017; Unuabonah and Taubert, 2014).

Recent studies of dye adsorption have shown that urea-cross-linked siloxane (ureasil)-polyether (U-PE) materials are efficient dye adsorbents (Bekiari and Lianos, 2006; Molina et al., 2014; Moura et al., 2015). Compared to mineral and polymeric materials in the form of powders, such as clays, manganese oxide, silica, alumina, and chitosan,

U-PE hybrid materials are easier to recover from wastewater due to their rubbery nature, flexibility, and insolubility in water (Santilli et al., 2009). Bekiari and Lianos (2006) synthesized ureasil-poly(oxypropylene) (U-PPO) with molar masses of 4000, 2000, and 230 g mol^{-1} and ureasil-PPO-block-poly-oxyethylene (PEO-block-PPO) with molar masses of 1900, 800, and 500 g mol^{-1}, for application in dye adsorption. The materials were shown to efficiently adsorb dyes, with the highest efficiency of adsorption of acid orange 7 dye achieved using U-PPO with molar mass of 230 g mol^{-1}. More recently, Molina et al. (2014) demonstrated that U-PEO with molar mass of 500 g mol^{-1} provided selective adsorption of anionic dyes, rather than cationic dyes. In other work, hybrid matrices composed of 3-glycidoxypropyl-tri-methoxysilane (GPMS) linked to end-group functionalized poly-etheramines (U-PEO and U-PPO) showed good adsorption capacity (415 mg g^{-1}) for the rose bengal anionic dye (Moura et al., 2015). Montmorillonite (Mt) is an efficient adsorbent of cationic dyes such as methylene blue (MB), crystal violet, methyl violet, basic blue 16, and others (Aladağ et al., 2014; Almeida et al., 2009; Fil et al., 2012; Gunay et al., 2013; Zhu et al., 2014). Dye adsorption by Mt. usually occurs by means of electrostatic interactions (Aladağ et al., 2014; Hegyesi et al., 2017).

In this work, we describe the development of a novel U-PEO hybrid nanocomposite with both anionic and cationic adsorption properties,

which can be easily recovered at the end of the adsorption process. The incorporation of sodium Mt. during the sol-gel synthesis of a U-PEO hybrid resulted in the formation of a rubbery sodium montmorillonite/ureasil-poly(oxyethylene) clay-polymer nanocomposite (CPN). The structural features of the hybrid nanocomposite were studied by X-ray diffraction and infrared spectroscopy. The evolution of the nanostructure during the adsorption process was investigated by *in situ* SAXS. The adsorption process was quantitatively monitored using UV–Vis spectroscopy.

2. Materials and methods

2.1. Synthesis of the hybrid precursor

A 10.4 mL volume of 3-isocyanatopropyltriethoxysilane (ICPTES) (Sigma-Aldrich, 95%) was mixed with 40 g of O,O′-bis(2-aminopropyl)-polypropylene glycol-block-polyethylene glycol-*block*-polypropylene glycol (molar mass = 1900 g mol^{-1}) (Fluka) in 150 mL of tetrahydrofuran (Synth) as solvent. The mixture was refluxed for 24 h at 78 °C. At the end of the reaction, the solvent was removed using rotary evaporation at 60 °C, producing the hybrid precursor (Santilli et al., 2009).

2.2. Incorporation of clay mineral in the hybrid matrix

A 0.3 g mass of Mt. (Southern Clay Products) was mixed with 3.0 mL of anhydrous ethanol (Sigma-Aldrich), under sonication (Vibracel VC 501) for 2 min to improve dispersion of the Mt. The dispersion was transferred to a beaker containing 1.5 g of the hybrid precursor and the sol-gel reactions were then induced by adding 100 μL of distilled water, under mechanical stirring for 4 h, followed by addition of 36 μL of 2 M HCl (Mallinckrodt) as catalyst. Drying at room temperature in a desiccator under vacuum resulted in disk-shaped monolithic xerogels ∼ 25 mm in diameter and ∼1 mm in height.

2.3. Characterizations

Fourier transform infrared spectroscopy (FTIR) analyses were performed using a Bruker VERTEX 70 instrument equipped with a DLaTGS detector and operated in attenuated total reflection mode. KBr pellets containing 1% (m/m) of sample were analyzed in the spectral range 4000–400 cm^{-1}, with 4 cm^{-1} resolution and 64 scans.

X-ray powder diffraction (XRD) was used to study the crystalline structure of the CPN and evaluate the intercalation and exfoliation of the Mt. dispersed in the U-PEO hybrid matrix. The XRD measurements were performed using a Siemens D5000 diffractometer operated with CuKα radiation (λ = 1.5405 Å) monochromatized using a curved graphite single crystal, 6.0 mm detector slits, and 2θ from 2 to 70°, with a 0.02° step every 3 s.

Methylene blue (Sigma-Aldrich) was used in the adsorption study as-received, without further purification. The evolution of the MB concentration in the supernatant solution during the adsorption process was monitored by UV–Vis absorption spectrophotometry using the MB monomer band (λ$_{max}$ = 665 nm). It is important to note that the UV–Vis spectra (Fig SI1, Supplementary information) of MB supernatant solution after the adsorption equilibrium display an invariant shape with a maximum at λ = 665 nm, a shoulder at λ = 615 nm corresponding to the vibronic transition and any evidence of the MB dimer band at 605 nm (Bergmann and O'Konski, 1963). Moreover, the ratio between the amplitude of the main band and the shoulder stays constant (A$_{665}$/A$_{615}$ = 2.0 ± 01), confirming the negligible contribution of MB dimer (λ$_{max}$ = 605 nm) to the MB monomer absorption spectra. Under this condition the concentration of the MB monomer could be determined from the experimental analytical curve presented in Fig. SI2. For the isothermal absorption experiments approximately 0.01 g portions of the CPN were immersed in 60 mL of aqueous solution

containing MB at different concentrations (∼ 4, 5, 6, 7, 8, 9, and 10 mg L^{-1}). The samples were agitated in a temperature-controlled reciprocating shaker bath at 25 °C for 36 h. During this period, the dye concentration (C_t) in the supernatant solution was analyzed at regular intervals using a Cary 60 UV–Vis spectrophotometer equipped with a 10 mm immersion probe. The mass of dye adsorbed per gram of CPN, q_t (mg g^{-1}), was calculated as a function of immersion time according to:

$$q_t = V \frac{(C_o - C_t)}{m} \tag{1}$$

where C_O is the initial dye concentration (mg L^{-1}), V is the dye solution volume (mL), and m is the CPN mass (g).

The nanostructures of the dry nanocomposites and their evolution during dye adsorption were monitored *in situ* using small angle X-ray scattering (SAXS). The measurements were performed at the SAXS 1 beamline of the National Synchrotron Light Laboratory (LNLS, Campinas, Brazil). For the adsorption process, the sample was placed in a liquid sample cell and 5 mL of aqueous MB dye solution was added with a syringe, at room temperature (25 ± 1 °C). A monochromatic beam (λ = 1.550 Å) and a bidimensional detector (PILATUS 300 K) located at a distance of 900.55 mm from the sample were used to measure the scattering intensity, I(q), according to the modulus of the scattering vector: q = (4π/λ) / sin(θ/2), where θ is the scattering angle and λ is the radiation wavelength. SAXS data were acquired during 4 s, every 26 s, during the first and the last hours of adsorption.

3. Results and discussion

3.1. Structural features

Fig. 1a shows a comparison of the infrared spectra of pristine MB, Mt., and U-PEO, together with those for the hybrid nanocomposites (CPN:MB and Mt.:MB) after dye adsorption (10 mg L^{-1}). The CPN:MB spectrum presented the characteristic U-PEO bands centered at 3355 (νNH, H-bonded), 2951 (ν$_a$CH$_2$), 2866 (ν$_s$CH$_3$), 1642, 1560, 1455 (CH$_2$ scissoring), 1347 (CH$_2$ wagging), 1241 (CH$_2$ twisting), 1092 (νCO), 1037 (νCO, νCC, rCH$_2$), 941 (νCC, rCH$_2$) and 844 cm^{-1} (νCO, rCH$_2$) (de Zea Bermudez et al., 1999). The weak band located at 3355 cm^{-1} is an overtone of the band at 1560 cm^{-1} attributed to the so called amides II, while the band at 1642 cm^{-1} is related to the so called amides I (Pavia et al., 2012). The absorption due to the symmetrical stretching vibration of the Si-O-Si of U-PEO siloxane nodes, occurring in the 950 to 1150 cm^{-1} range, are masked by the very intense C−O stretching absorption (1092 cm^{-1}) and the strong coupled vibrations of the C−C stretching and CH$_2$ rocking (1037 cm^{-1}) modes that fall in the same range of frequencies (de Zea Bermudez et al., 1999).

The presence of the Mt. in the Mt.: MB and CPN:MB samples was evidenced by the characteristic Mt. bands located at 3625, 516, and 448 cm^{-1} (Madejová, 2003; Validi et al., 2012). The band at 3625 cm^{-1} was assigned to the stretching vibration of structural OH bonded to Al or Mg. Bands at 516 and 448 cm^{-1} were assigned to Al-O-Si and Si-O-Si bending vibrations, respectively (Chieng et al., 2010; Validi et al., 2012). Comparison of the CPN:MB and Mt.:MB spectra to the MB spectrum revealed major changes, as shown for the amplified 900–1700 cm^{-1} region (Fig. 1b). The band centered at around 1383 cm^{-1} in the MB spectrum, attributed to the C=S bond (Kariminezhad et al., 2015), appeared at 1391 cm^{-1} and 1385 cm^{-1} in the CPN:MB and Mt.:MB spectra, respectively. Similarly, the band located at 1590 cm^{-1} in the dye spectrum, assigned to aromatic ring C=C vibration (Àngels Olivella et al., 2012; Validi et al., 2012), was shifted to higher energies of 1600 and 1605 cm^{-1} in the CPN:MB and Mt.:MB spectra, respectively. The band centered at 1484 cm^{-1} in the dye spectrum, attributed to symmetric C=N stretching vibration (Feng et al., 2013; Validi et al., 2012), showed blue shifts to 1487 and 1498 cm^{-1} in the CPN:MB and Mt.:MB spectra, respectively. These shifts indicate the existence of strong interactions between the MB dye