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Research paper

Preparation of nanocomposites for the removal of phenolic compounds from aqueous solutions

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ABSTRACT

Alginate beads, with and without different types of organo-modified clays, were obtained using a calcium chloride (CaCl₂) solution. Firstly, raw clays were organo-modified with a cationic surfactant, hexadecyl trimethylammonium (HDTMA). Then, their cationic exchange capacities (CEC) were calculated and they also were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Afterwards, the obtained polymers and clay polymer nanocomposites (CPN) were carefully characterized by means of the same techniques. Later, different phenol and 4-chlorophenol (4CF) aqueous solutions were prepared and put in contact, for different periods of time, with the synthesized CPN. Phenol and 4CF concentrations were measured by means of UV–vis spectroscopy. Results indicated a successful modification of the raw clay with this cationic surfactant and its incorporation into the alginate polymer matrix. Finally, the maximum removal capacities for both phenolic compounds, 4CF and phenol, were found at $q_e = 0.334 \text{ mg}\cdot\text{g}^{-1}$ and $q_e = 0.118 \text{ mg}\cdot\text{g}^{-1}$, respectively.

1. Introduction

Nowadays, new challenges are being faced for the development of adsorbent materials that are able to cover the expectations of sustainability and maximum efficiency in the processes of water treatment. One type of material has been studied: composites, which consist of the combination of two or more chemically distinct and insoluble phases that are joined, and their properties and structural performance are superior to those of their constituents acting individually. One of the most studied composite systems is the clay polymer nanocomposite (CPN) (Sinha Ray, 2013). These are classified according to the interactions between the polymer matrix and the silicate layers filler (Sinha Ray, 2013; Gacitua et al., 2005; Pavlidou and Papaspyrides, 2008; Bergaya et al., 2011; Anadão, 2012; Bergaya and Lagaly, 2013; Bergaya et al., 2013): a) intercalated nanocomposites; they are formed when one or more polymer chains, with a well-ordered distribution, are intercalated in an interlayered space of a clay. The stacking of the layers is preserved, with the order along the *c*-axis; the result is a multilayered structure of alternating polymer chains and clay layers with some

distance between them; b) exfoliated nanocomposites; these materials are obtained by the total separation of the individual layers of the clay, in a disordered-fashion dispersion of the individual clay layers, in the polymer matrix; finally, c) microcomposites, which are dispersions of fine, micro-sized clay mineral particles in the polymer matrix. Fig. 1 shows the different types of CPN.

The traditional processes to prepare nanocomposites using layered compounds such as reinforcement, especially clays, can be summarized as follows (Biswas and Sinha Ray, 2001; Sinha Ray and Okamoto, 2003; Gacitua et al., 2005; Anadão, 2012): a) exfoliation-adsorption, also called dispersion in solution, the silicate is exfoliated in individual layers in a solvent in which the polymer or prepolymer is soluble (water, toluene, etc.); b) *in situ* polymerization, a monomer solution is used as medium for the clay dispersion, and under specific conditions, the polymerization is induced in the interlayer space; and finally, c) melting intercalation, in this method, the silicate is mixed with a thermoplastic polymer matrix in the molten state. Under these conditions, the polymer is carried through the interlayer spaces forming a nanocomposite. Fig. 2 illustrates these methods of nanocomposites synthesis.

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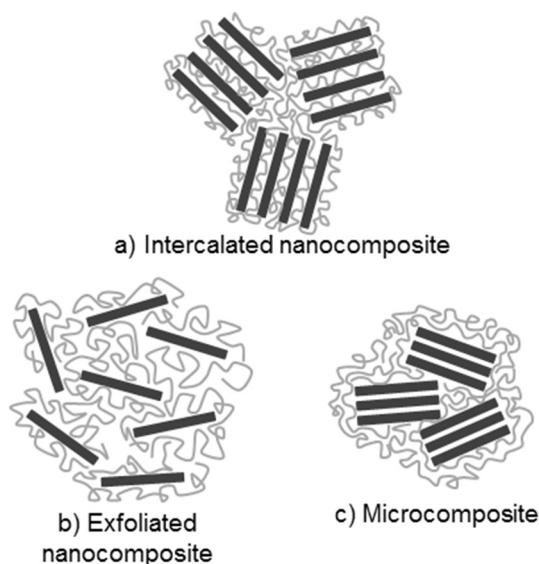


Fig. 1. Structures of the different synthesized clay polymer nanocomposites (CPN).

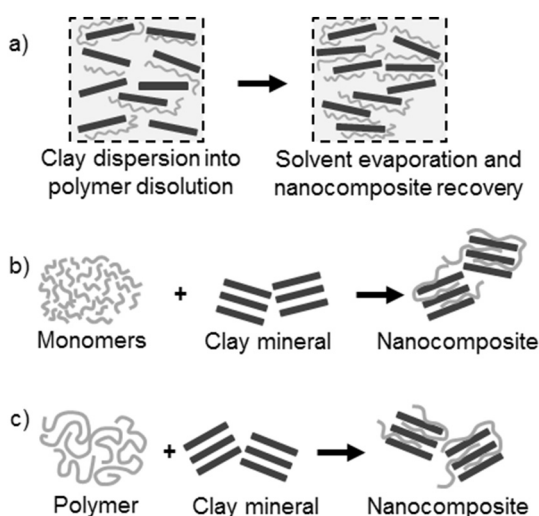


Fig. 2. Different processes for the preparation of CPN.

On the other side, sodium alginate has been recently used in environmental applications, most important for the removal of organic compounds from wastewaters (Feng et al., 2017; Munagapati and Kim, 2017; Pandey et al., 2017; Zhiyu et al., 2017). This polymer shows a sol-gel transition, when its cations are exchanged; namely, when a divalent cation such as calcium is exchanged for two monovalent cations, like sodium. One of the most notable features of alginate is its biocompatibility, as well as its preparation. Moreover, alginate beads are well known for their applications in composites science, as an encapsulant in biomedicine or as a support of different clay materials, like montmorillonite (Mt).

Mt. has been used as a support of alginate beads, because of the improvement on the mechanical properties of the polymer matrix, and because of the simplicity on its organo-modification procedure for the removal of pesticides or polychlorinated biphenyl compounds (PCB) (Silva et al., 2008; Cavallaro et al., 2013; Barreca et al., 2014).

In the present work, the properties of clay alginate nanocomposites were evaluated for the removal of two different compounds, phenol and 4-chlorophenol (4CF), from aqueous solutions. For this purpose, three different types of Mt. were used for the synthesized composites. The first one, an Mt. raw mineral from Puebla State (a Mexican province); the second one, an organo-modified Mt. with hexadecyl trimethylammonium

ions (HDTMA); and the third one, a commercial clay modified with dialkyl dimethylamine ions (C_{14} - C_{18}). Their morphology and their thermal and spectroscopic characteristics were evaluated, their maximum adsorption capacities were calculated, and their kinetics adsorption models were studied.

2. Experimental

2.1. Materials

All the chemicals and materials used in the synthesis and characterization of clay alginate nanocomposites, as well as those for the phenolic compounds adsorption tests were used as received without any further purification, unless otherwise stated. Sodium alginate (SA), anhydrous sodium acetate (SAc, $CH_3COO^-Na^+$, FW = 82.03 g/mol, $T_b = 337^\circ C$) and phenol (C_6H_5O , FW = 94.11 g/mol, $T_b = 182^\circ C$, $T_m = 43^\circ C$) were obtained from Meyer. Hexadecyl trimethylammonium bromide (HDTMA-Br, FW = 364.45 g/mol, $T_m = 212^\circ C$), a synthetic Mt. organo-modified with dialkyl dimethylamine (C_{14} - C_{18} , FW = 180.1 g/mol, apparent density = 600–1100 kg/m^3 , particle size < 20 μm), identified as B3 nanoclay, and 4-chlorophenol (4CF, C_6H_4ClO , FW = 128.56 g/mol, $T_b = 220^\circ C$) were obtained from Sigma-Aldrich. Calcium chloride ($CaCl_2$, FW = 110.98 g/mol, $T_m = 772^\circ C$) and potassium chloride (KCl, FW = 74.55 g/mol, $T_m = 776^\circ C$) were obtained from JT Baker. Finally, two commercial Mt. raw minerals from Puebla State identified by the supplier as B1 and B2 were used.

2.2. Natural clay organo-modifications and cationic exchange capacities (CEC)

The organo-modification of the Mt. raw minerals and their cationic exchange capacities (CEC) were calculated according to the modified Ming and Dixon method (Díaz-Nava et al., 2012). Namely, 25 g of the Mt. raw mineral (B1 or B2) were weighed and placed into a flat bottom ball flask; then, 250 mL of an HDTMA solution (25 $eq \cdot L^{-1}$ or 50 $eq \cdot L^{-1}$) were added, and magnetically stirred for 15 min. Afterwards, the flask was placed in a shaker bath at 30 $^\circ C$ and 100 rpm for 48 h. Next, the supernatant was removed by decantation and the Mt. was washed with deionized water at 30 $^\circ C$; a bromide test was performed for each wash until the test resulted negative (6 washes of 200 mL). Subsequently, the Mt. was dried at 70 $^\circ C$ for 24 h, was milled and was passed through a 400 mesh screen to obtain a particle size of 37 μm . Finally, materials were labeled as B1–250 and B2–250 (materials modified with 250 $eq \cdot g^{-1}$) or B1–500 and B2–500 (materials modified with 500 $eq \cdot g^{-1}$).

2.3. Clay alginate nanocomposites synthesis

CPN were synthesized according to the next procedure: a solution “A” consisting of 1 g of SA was dissolved in 50 mL of deionized water at 60 $^\circ C$ for 2 h, with magnetic stirring. On the other hand, a solution “B” which consists of 5 g of B1–250, B1–500, B2–250, B2–500 or B3 Mt. were dispersed in 50 mL of deionized water using an ultrasound bath at 30 $^\circ C$ for 2 h. Afterwards, clay dispersions were poured into the SA solution, and magnetic stirred at 30 $^\circ C$ for other 2 h. Then, mixtures were dripped into 500 mL of a 0.1 M $CaCl_2$ solution by means of a peristaltic pump and a micropipette tip. Finally, the obtained beads were agitated for 2 h and refrigerated for 24 h.

2.4. Characterization

2.4.1. Natural and/or organo-modified clays and CPN

X-ray diffraction (XRD) analyses were performed on a Rigaku X-ray diffractometer; model Ultima IV, with the powder method. Samples were run from 1 $^\circ$ to 70 $^\circ$ in 2θ , with a step size of 0.020 $^\circ$ and with a speed of 1.5 $^\circ$ /min.

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