Journal of Environmental Management 221 (2018) 28–37

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Functional polyaniline/multiwalled carbon nanotube composite as an efficient adsorbent material for removing pharmaceuticals from aqueous media

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ARTICLE INFO

Keywords:
Adsorption
Multiwalled carbon nanotube
Pharmaceuticals
Polyaniline
Polymer composite
Removal

ABSTRACT

The composite polyaniline/multiwalled carbon nanotube (PAni/MWCNT, 1:0.1 *w/w*) was developed with the intention of binding the adsorbent properties of two materials and using it to adsorb pharmaceuticals from aqueous media. PAni/MWCNT was characterized by scanning electron microscopy, thermogravimetry, infrared spectroscopy, pH at the point of zero charge, and the effect on the surface wettability of the material. As proof of concept, adsorption studies were carried out using meloxicam (MLX) as the pharmaceutical and it was evaluated as a function of pH, temperature, ionic strength, contact time and variation in concentration. Kinetics and isothermal models were applied to evaluate the mechanism of the adsorption process. The best MLX adsorption result was at pH 2 with 6 min of contact with PAni/MWCNT. The kinetics models that fitted the experimental data were pseudo-second order and Elovich and the kinetics model was the dual-site Langmuir–Freundlich. Both models suggest that the adsorption occurs by the chemical nature of the surface and in the pores of the energetically heterogeneous composite. The PAni/MWCNT presented an adsorption capacity of 221.2 mg g^{-1}, a very good value when compared with the literature and can be used to remove pharmaceuticals from aqueous environments.

1. Introduction

The science and technology of new materials have attracted much attention for the last few years and an expectation as to the impact they cause in several areas. Research, innovation, and development of new adsorbent compounds are gaining significant space in the area of materials chemistry for improvements in their physical and chemical properties making them more and more efficient. An example of the quality of materials is a composite preparation. Composites represent a class of materials in which two or more substances are combined to exhibit unique properties, which are the result of the sum of their individual components (Oliveira et al., 2006).

The adsorbent materials have some specific characteristics, such as an insoluble solid surface, generally porous and with a large surface area. Because of these characteristics they are able to effect on their surface the adhesion of organic or inorganic molecules dispersed in liquid or gaseous medium by their wide affinity for different interactions (IUPAC, 2015). This adhesion of molecules is a surface phenomenon known as adsorption on the adsorbent (solid), which is dependent on the physicochemical characteristics and the nature of the aqueous medium, such as solubility, pH, viscosity, temperature, contact time and concentration.

Some examples of adsorbent materials are carbon nanotubes (CNTs) and polymers. CNTs are hollow cylindrical molecules of nanometer scale, composed of carbons bonded together with sp^2 hybridization (Zhang et al., 2010). These compounds may have different structures and sizes according to their synthesis: they can be obtained in a single-walled (SWCNT) or in multiwalled carbon nanotube (MWCNT). Because of the structure of the CNTs being highly porous, hollow, and having a large surface area, they show strong interaction with the desired analyte, for example, pharmaceuticals (Zhang et al., 2010). Some examples of CNTs utilization are the removal of heavy metal ions in the environment and adsorption of molecules in solution, by means of electrostatic forces, hydrogen bonds, π–π and hydrophobic interactions (Pérez et al., 2010; Ren et al., 2011; Samanidou and Karageorgou, 2012).

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https://doi.org/10.1016/j.jenvman.2018.05.051
Received 19 January 2018; Received in revised form 9 May 2018; Accepted 16 May 2018

One class of the synthetic polymers is conductive polymers, in which polyaniline (PAni) is an example. PAni has conjugated π bonds in the polymer chain and has chemical and physical properties that enable them in various applications, such as electrodes, sensors, rechargeable batteries, and recently as adsorbent material in sample preparation (Bhadra et al., 2009; Bagheri et al., 2013). The idea of adding the MWCNT in the PAni synthesis is to improve the adsorption capacity of the composite due to the sum of the adsorptive properties of the two separated materials, as already reported in the literature, and also to evaluate the adsorption capacity of pharmaceutical compounds (Ansari et al., 2017).

Environmental fate and potential ecological harm of the active ingredients in pharmaceuticals have received much attention, and among them, the nonsteroidal anti-inflammatory drugs (NSAIDs) are widely prescribed and used. Meloxicam (MLX) is an NSAID used to alleviate pain and inflammation and is indicated for the treatment of the symptoms of rheumatoid arthritis and osteoarthritis (Busch et al., 1998). This class of drugs is commonly consumed worldwide because it relieves pain and does not require a medical prescription. In addition, some unspent active ingredients and metabolic byproducts are excreted from the users' bodies ending up in the municipal wastewater collection and treatment systems. It is of fundamental importance to quantify and to qualify these drugs in the environmental scope because if they are outside the limit, they become harmful to human and animal health. Therefore, the discovery of new adsorbent materials for use in sample preparation techniques is essential for analytical methodologies to be more efficient, fast, accurate, and low cost.

Therefore, the idea of this work was to use a composite that binds the adsorptive capacity of two adsorbent materials of low cost and efficiently removes pharmaceuticals from an aqueous medium. Then, the PAni/MWCNT composite was prepared to remove pharmaceuticals from aqueous media and MLX was used as proof of concept. PAni/MWCNT was characterized by infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetry (TG), pH at the point of zero charge (pH_{PZC}) and the effect on the surface wettability of the material. In the adsorption studies, the parameters of pH, temperature, ionic strength, time, and concentration were evaluated and applied in kinetics (pseudo-first order, pseudo-second order, Elovich, and intraparticle and film diffusion) and isothermal models (Langmuir, Freundlich, Sips, single-site Langmuir–Freundlich, and dual-site Langmuir–Freundlich) to understand the adsorption mechanism of MLX in the composite in aqueous medium.

2. Experimental

2.1. Obtaining and preparing adsorbent material

PAni/MWCNT composite was synthesized in two ways to evaluate and choose the best mass ratio of aniline monomer and MWCNTs, in which the ratios of 1:0.1 and 1:1 were tested. Therefore, 0.2 and 2.0 g of MWCNTs (99%, from Nanocyl®) each containing 80 mL of hydrochloric acid Vetec® (1 mol L^{-1}) were placed separately in two beakers and left in an ultrasonic bath for 15 min. Then, 2 mL of aniline monomer (99.5% from Sigma-Aldrich®) previously distilled was added to each beaker and allowed to stir for 30 min. These solutions were conditioned in an ice bath and 80 mL of 0.33 mol L^{-1} ammonium persulfate solution (Synth®) was dripped in with vigorous stirring for a further 5 h. The resulting greenish-black precipitates in the two syntheses were vacuum filtered and washed extensively with Milli-Q water and hydrochloric acid (1 mol L^{-1}) and finally dried in the oven at 60 °C for 24 h. The yields of the two syntheses were approximately 97%, and the materials were evaluated by FTIR for the choice of the best aniline monomer and MWCNTs ratio, with the ratio 1:0.1 being chosen.

2.2. Adsorbent characterization

The composite was characterized by techniques of SEM, FTIR, and TG, by pH_{PZC} and also by tests with hydrophobic/hydrophilic material. The TG analyses were performed by the thermobalance Shimadzu DTG-60H, with a heating rate of 10 °C min^{-1} between 25 and 1000 °C under nitrogen flow (50 mL min^{-1}), an inert atmosphere. The FTIR analyses were performed on a PerkinElmer FTIR Spectrum GX, operating between 4000 and 400 cm^{-1} with resolution of 4 cm^{-1}, using the KBr tablet method. The SEM images were obtained on a Hitachi Analytical Microscope TM3000 Table Top with an acceleration voltage of 15 kV imaging.

The pH_{PZC} was performed by placing 50 mg of PAni/MWCNT in Falcon® tubes and adding 20 mL of water with pH values between 2 and 10 (initial pH), which were adjusted with solutions of HCl and NaOH to 0.05 mol L^{-1} and measured with a pH meter. The tubes were shaken at 200 rpm for 10 min, allowed to stand for 24 h, and after that time the pHs of the solutions (final pH) were measured. The initial and final pH values were plotted on the final pH *vs* initial pH plot and pH_{PZC} was found at the point where the final pH was equal to the initial pH.

The tests on hydrophobic/hydrophilic material PAni/MWCNT was performed by wettability studies, which usually involve the measurement of angles, which indicates the degree of wetting when a solid and liquid interact (Lu et al., 2017; Yuan and Lee, 2013). To do this, the material was dried at 60° for 24 h to remove any water present, a drop of water was placed on the flat surface of the material, and then the angle value was measured. If the angle was less than 90°, the material is hydrophilic, if the angle is greater than 90°, the material is hydrophobic (Yuan and Lee, 2013).

2.3. Instrument of analysis

High-performance liquid chromatography coupled with diode array detector, model 1290 (HPLC-UV) from Agilent® (Agilent Technologies, Palo Alto, CA, USA), consisted of a quaternary pump, thermostat, autosampler, and column oven. This equipment was used for the adsorption tests of MLX in aqueous medium. The data were controlled by Agilent Open LAB Chromatography Data Software System®.

2.4. Adsorption experiments

The adsorption studies were realized using 17.5 mg of PAni/MWCNT in a test tube and 3.5 mL MLX added (99.7%, United States Pharmacopeia Reference Standard, USP) aqueous solution 0.1 mg mL^{-1} to pH and time contact studies and 3.0 mg mL^{-1} to concentration study, prepared from stock solution of MLX 5.0 mg mL^{-1} in methanol (J.T. Baker®). In this study were evaluated the influence of the pH, temperature, ionic strength, contact time and concentration, being that the adsorption mechanism were investigated by kinetics and isotherm models. Equation (1) was used to calculate the amount of MLX adsorbed onto the composite.

$$q_e = \frac{(C_i - C_f)V}{m}, \quad (1)$$

where q_e is the amount MLX adsorbed (mg g^{-1}); C_i and C_f are the initial and final concentrations of MLX, respectively (mg L^{-1}), determined by HPLC-UV; V is the volume of solution (L); m is the mass of the polymer composite (g) (Fonseca et al., 2015).

2.4.1. Adsorption studies at different pH

The adsorption of MLX in the PAni/MWCNT was evaluated in a wide pH range 2–10. The pH was adjusted to the desired value using 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} HCl. Then, the solutions of the adjusted pH were added to test tubes containing PAni/MWCNT. The tubes were agitated on a vortex for 2 min at 2000 rpm and after that they were centrifuged at 1500 rpm for 2 min. The supernatant was