New adsorbent for diclofenac based on bentonite

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INTRODUCTION

Diclofenac is an emerging pollutant widely detected in aquatic environments, and adsorption is considered an effective technique for its removal (Sathishkumar et al., 2020; Aminul Islam et al., 2024; Fraiha et al., 2024). In this context, this work investigates the use of tin-modified bentonite (Sn-Bent) as an adsorbent for the removal of diclofenac.

METHODS

The Sn-Bent sample was synthesized by reacting sodium bentonite (Na-Bent), supplied by Bentonisa Company, Brazil, with a cation exchange capacity (CEC) of 74.6 cmol(+) kg^{-1}, and a chemical composition of SiO_2 (52.98%), Al_2O_3 (18.35%), Fe_2O_3 (3.96%), TiO_2 (0.18%), CaO (0.01%), MgO (2.47%), Na_2O (2.56%), and K_2O (0.22%) (Brito et al., 2018), with a 0.01 mol L^{-1} $SnCl_2$ solution for 24 h. Adsorption was carried out following previous method (França et al., 2020) by mixing a fixed mass of the adsorbent in 25.0 mL of the drug solution in an initial concentration in a fixed pH and contact time at 25 °C under orbital agitation. The influences of pH (6.0-8.0), adsorbent dosage (10-150 mg), time (5-120 min), and initial drug concentration (5-100 mg L^{-1}) were evaluated in a single-parametric study. The pH tests were carried out under the same conditions for the crystalline SnO_2 for control and the solids were characterized by X-ray diffraction (XRD) at the SGI X-ray Laboratory - Research, Technology and Innovation Center of the University of Seville (CITIUS), and by Fourier Transform Infrared Spectroscopy (FTIR) at the Fuel and Materials Laboratory (NPE – LACOM) at the Federal University of Paraíba.

RESULTS

The Na-Bent XRD pattern exhibited a reflection at $2\theta = 7.03°$, corresponding to the (001) plane of a sodium smectite with a basal spacing of 1.26 nm, together with additional reflections at $2\theta = 14.2°$, 19.8°, 28.3°, 35.0°, 53.9°, and 61.9°, the latter attributed to the (060) plane of a dioctahedral smectite, according to PDF cards 00-058-2038 and 00-058-2039, as well as the literature (Moore and Reynolds, 1989; Brito et al., 2018). Bentonite, composed predominantly of montmorillonite (≥50%), a 2:1 phyllosilicate (Brigatti et al., 2013), also contains common impurities such as gypsum, quartz, and anorthite, consistent with natural clay compositions (Santos et al., 2024). XRD patterns revealed the presence of hydrated SnO_2 or $Sn(OH)_4$ nanoparticles in the Sn0.01-Bent sample, with a base spacing of 1.50 nm, indicating the successful intercalation of Sn species in the clay mineral structure (Masui et al., 2014; Baranowski et al., 2019). Rietveld refinements showed 12.8% SnO_2 content in the Sn0.01-Bent. FT-IR spectra exhibited significant shifts in the O-H stretching bands (from 3440 cm^{-1}) (Slaný et al., 2019; Madejová et al., 2021; Oliveira et al., 2021), as well as in the water deformation band (from 1641 cm^{-1} to 1630 cm^{-1}) (Slaný et al., 2019), suggesting that hydrogen bonding occurred between SnO_2 nanoparticles and the surface of the clay mineral (Kiricsi et al., 1994). The presence of new adsorption sites enhanced the adsorption of diclofenac. The adsorption

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isotherms showed that the adsorption capacity for diclofenac was 65.1 mg g^{-1}, while no adsorption was observed for the pristine sample.

DISCUSSION

The adsorption mechanism was investigated by FTIR analysis, which indicated that the tin modification of montmorillonite phase introduced new active sites that interact specifically with the diclofenac molecule. This interaction, including the formation of complexes between the carboxylate group of diclofenac and the Sn(IV) species, is likely the mechanism behind the observed adsorption.

CONCLUSIONS

Sn-modified bentonite behaved as an effective adsorbent for diclofenac from water, offering a promising solution for addressing environmental pollution.

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