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Pesticides adsorption–desorption on Mg–Al mixed oxides. Kinetic modeling, competing factors and recyclability

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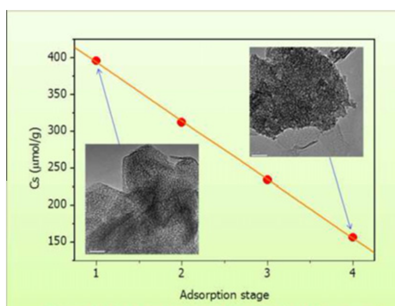
HIGHLIGHTS

- ▶ Adsorption of Nicosulfuron and Mecoprop-P on calcined hydrotalcite (HT500).
- ▶ Kinetic data showed that their adsorption involves intraparticle diffusion.
- ▶ The adsorption is favorable and occurs via an exchange of ions.
- ▶ The adsorption is affected by the presence of ions such as PO_4^{3-}, SO_4^{2-}, and CO_3^{2-}.
- ▶ The extraction of pesticides with CO_3^{2-} suggests that the adsorbent can be recycled.

GRAPHICAL ABSTRACT



Changes in the morphology of the particles after several adsorption-desorption cycles

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ABSTRACT

The adsorption of the ionizable pesticide Nicosulfuron and the ionic pesticide Mecoprop-P on a calcined Mg–Al hydrotalcite (HT-500) in the presence and absence of various anions was studied with a view to assessing the potential of regenerating the adsorbent. Kinetic tests showed the adsorption of both pesticides to involve intraparticle diffusion, and the rate constant of intraparticle diffusion for Nicosulfuron to increase with increasing concentration of the compound by effect of its increased molecular size relative to Mecoprop-P. Application of the Langmuir and Dubini–Radushkevich equations to the adsorption isotherms for the two pesticides revealed easy adsorption of both via an ion-exchange process. Adsorption and desorption of the two pesticides were both affected by the presence of other anions. The adsorbents and their adsorption products were characterized by X-ray diffraction and FT-IR spectroscopies. Based on the results of regeneration tests, calcined hydrotalcite is an effective adsorbent for the removal of Nicosulfuron and Mecoprop-P from contaminated water.

1. Introduction

Pesticides are very hazardous pollutants that can persist in the aquatic environment for many years [1]. Contamination of soil and ground water by pesticides applied to soil and swept by transport processes such as leaching or runoff is a posing an increasingly serious environmental problem.

Some researchers have suggested that the use of layered double hydroxides (LDHs), also known as “anionic clays” or “hydrotalcite-like compounds” (HTs), as filters for pesticide-contaminated water or additives in controlled-release pesticide formulations might be effective toward partially or completely avoiding the environmental impact of pesticides [2–4]. LDHs are brucite-like layered materials of general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}X^{n-}_{x/n} \cdot mH_2O$, where M^{II}

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and M^{III} are a divalent and a trivalent cation, respectively, and X^{n-} is an interlayer anion countering the positive charge arising from the presence of M^{III} in the layers. Layer charge in an LDH is dictated by the mole ratio $M^{III}/(M^{III} + M^{II})$, which typically ranges from 0.2 to 0.4 [5,6]. The main interest of these materials lies in their structure, high anion-exchange capacity and straightforward synthesis [3,7–9].

The adsorption efficiency of LDHs is strongly affected by the properties of their interlayer anions [10]. Thus, LDHs usually have a greater affinity for anions with a high charge density and hence tend to adsorb multivalent anions easily in relation to monovalent ions [11,12]. In addition, LDHs exhibit preferential affinity for CO_3^{2-}, which usually hinders further ion-exchange [13]. However, interlayer CO_3^{2-} ions can be removed by heating LDH at about 500 °C to obtained calcined LDH (HT500), which can regain the original LDH structure in the presence of dissolved anions [14–16]:

$$Mg_3AlO_4(OH) + 4H_2O + (1/n)X^{n-} \rightarrow [Mg_3Al(OH)_8]X^{n-}_{1/n} + OH^-$$

where X^{n-} is the anionic species present in solution.

The anion-exchange capacity (AEC) of HT500 was much higher than that of the original LDH (5.8 vs 3.3 mmol g^{-1}) [17]; this allows the adsorption efficiency of an LDH to be significantly increased by calcination [16,18].

The influence of various common inorganic anions on pesticide adsorption is one other major factor to be considered since some such anions are often encountered in pesticide-contaminated waters [10].

Several author have studied different properties of Mecropop and Nicosulfuron pesticides such as their degradation or its effect in the grown of different vegetables. It had been studied adsorption and desorption of Nicosulfuron in soils [19,20] and clay minerals [21]. Furthermore, it had been studied the adsorption of Mecoprop on calcareous and organic matter amended soils [22], in clays [23] or onto Iron Oxides [24]. Also, Khan et al. [25] have characterized the Mecoprop-LDH hybrid synthetized by the cooprecipitation method.

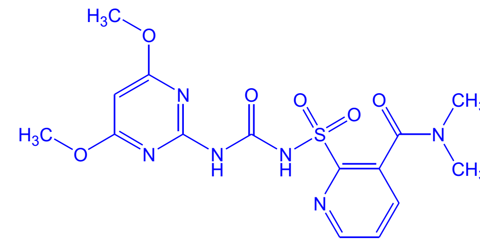
In this work, we examined the adsorption of two widely used, ionizable pesticides (Nicosulfuron and Mecoprop-P) on a calcined hydrotalcite (HT500) with a view to elucidating their adsorption–desorption behavior and the way it is influenced by the presence of some anions. In addition, we subjected the hydrotalcite to repeated adsorption–calcination cycles in order to assess its reusability in the removal of Nicosulfuron and Mecoprop-P from contaminated water.

2. Materials and methods

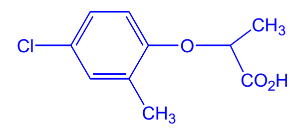
2.1. Pesticides

Nicosulfuron (2-[(4,6-dimethoxypyrimidin-2-ylcarbamoyl)sulfamoyl]-N,N-dimethylnicotinamide) and Mecoprop-P [(*R*)-2-(4-chloro-*o*-tolyloxy)propionic acid] were both supplied as high-purity products by Sigma–Aldrich. These pesticides are typically used to control weeds in post-emergence treatments. Nicosulfuron is a sulfonylurea of molecular weight 410.41 g mol^{-1}, a high solubility in water (7500 mg L^{-1} at 20 °C) and pK_a = 4.78. Mecoprop-P is an aryloxyalkanoic acid pesticide of molecular weight 214.65 g mol^{-1}, water solubility 860 mg L^{-1} and pK_a = 3.86. The structural formula of these pesticides is as follows:

NICOSULFURON



MECOPROP-P



2.2. Synthesis of the hydrotalcite, and characterization of the adsorbent and adsorption products

A hydrotalcite intercalated with carbonate anions and designated MgAl-LDH was prepared according to Reichle [7]. To this end, a solution containing 0.75 mol of $Mg(NO_3)_2{\cdot}6H_2O$ and 0.25 mol of $Al(NO_3)_3{\cdot}9H_2O$ in 250 mL of distilled water was dropped over 500 mL of another containing 1.7 mol of NaOH and 0.5 mol of Na_2CO_3 under vigorous stirring for 2 h. The resulting suspension was hydrothermally treated at 80 °C for 24 h, and the precipitate thus formed washed with distilled water and dried at 60 °C to obtain the solid MgAl-LDH, calcination of which at 500 °C for 3 h gave an Mg–Al mixed oxide that was named HT500.

The adsorbent (HT500) and adsorption products were characterized from their XRD patterns as obtained on a Siemens D-5000 diffractometer using Cu Kα radiation (λ = 1.54050 Å) and their FT-IR spectra as recorded by using the KBr disc technique on a Perkin Elmer spectrophotometer. The materials were also characterized microstructurally with a JEOL 200CX TEM instrument.

Elemental analyses (Mg and Al) were performed by atomic absorption spectrometry on a Perkin Elmer AA-3100 instrument, and C and N contents determined with a Eurovector 3A 2010 elemental analyzer.

2.3. Adsorption–desorption tests

Kinetic adsorption and adsorption–desorption isotherms for Nicosulfuron and Mecoprop-P were obtained by using the batch equilibration method. For kinetic adsorption, 30 mg of adsorbent for Nicosulfuron and 20 mg for Mecoprop-P were equilibrated in duplicate by shaking with 30 mL of pesticide solutions containing 0.25–1.0 mM Nicosulfuron and 1.0–3.0 mM Mecoprop-P at room temperature in a turn-over shaker operating at 52 rpm for variable lengths of time. For adsorption–desorption isotherms, duplicate samples containing 30 mg of adsorbent for Nicosulfuron and 20 mg for Mecoprop-P were equilibrated by shaking with 30 mL of 0.5–1.5 mM Nicosulfuron and 0.5–3.0 mM Mecoprop-P at room temperature for 24 h [26]. The resulting supernatant was centrifuged and separated to determine the concentrations of