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Removal of herbicides from aqueous solutions by modified forms of montmorillonite

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ABSTRACT

This investigation for the removal of agricultural pollutants, imazaquin and atrazine was conducted using montmorillonite (MMT) exchanged with organic cations through ion exchange. The study found that the adsorption of the herbicides was affected by the degree of organic cation saturations, the size of organic cations and the different natures of the herbicides. The modified clays intercalated with the larger surfactant molecules at the higher concentrations tended to enhance the adsorption of imazaquin and atrazine. In particular, the organoclays were highly efficient for the removal of imazaquin while the adsorption of atrazine was minimal due to the different hydrophobicities. Both imazaquin and atrazine were influenced by the changes of pH. The amphoteric imazaquin exists as an anion at the pH 5–7 and the anionic imazaquin was protonated to a neutral and further a cationic form when the pH is lower. The weak base, atrazine was also protonated at lower pH values. The anionic imazaquin had a strong affinity to the organoclays on the external surface as well as in the interlayer space of the MMT through electrostatic and hydrophobic interactions. In this study, the electrostatic interaction can be the primary mechanism involved during the adsorption process. This study also investigated a comparative adsorption for the imazaquin and atrazine and the lower adsorption of atrazine was enhanced and this phenomenon was due to the synergetic effect. This work highlights a potential mechanism for the removal of specific persistence herbicides from the environment.

1. Introduction

The security of surface and groundwater from pollution is a growing concern in many areas of the world [1]. A lot of attention has been paid to environmental problems associated with the presence of contaminants, including inorganic (e.g. heavy metals) and organic compounds (e.g. herbicides and pesticide, and polycyclic aromatic hydrocarbons (PAHs)) derived from agricultural and industrial activities in water. In the agricultural industry, atrazine is a type of triazine herbicide that is widely used as a plant-protecting agent [2–4], while imazaquin is an imidazolinone class herbicide that is designed to control weeds in soybeans [5–7] (see Fig. 1). The use of the agrochemicals to control organisms is a current concern as they dissolve in the soil and exacerbate the risk associated with runoff to surface and groundwater [8–12]. Hence, the attention researchers have been drawn to these public health and environmental concerns and the need to improve the quality of groundwater, especially, in areas where the loading of these compounds occurs [13].

To resolve this issue, many studies have been conducted to develop inexpensive, effective and efficient methods to remediate water from pollution without producing secondary pollutants by the treatment [13]. One treatment technique suggested in this study is the adsorption process, which has relatively lower operational cost, ease of operation and low tendency for the production of toxic secondary products [14].

Clay minerals and modified clay minerals are good candidate adsorbents for the remediation of environmental contaminants due to their unique features [15]. Clay minerals are abundant in nature, and possess layered structure and ion exchange properties, which enhance the modification of their surfaces with organic cations in order to increase their affinity for organic pollutants [16–19]. Replacement of inorganic exchangeable cations (Na^+ or Ca^{2+}) with organic cations yields hydrophobic organoclays and this simple modification is widely used to improve the adsorptive capacity of clays for hydrophobic organic compounds. Quaternary ammonium cations (QACs) are one of the commonly used organic cations for such modifications and many previous studies have investigated in the development of modified clays with non functionalised QACs or functionalised QACs for the adsorption of organic compounds [19–22]. Results from these studies indicate that the

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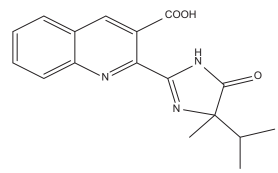
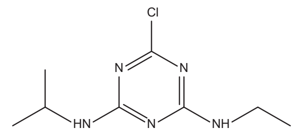
Chemical structure

Imazaquin



Atrazine



	Imazaquin	Atrazine
Log K_{ow} [1]	4.3 (at pH 4), 0.026 (at pH 7)	2.68
Solubility	60 mg/L at 25 °C	33 mg/L at 25 °C

[1] Octanol-water partition coefficients

Fig. 1. Molecular structures and properties of herbicides (a) imazaquin and (b) atrazine.

selection of the organic cations is critical to the performance of organoclays for the removal of organic pollutants.

Hence, in this research, the potential use of organoclays as adsorbents was investigated for the removal of two different forms of herbicides; imazaquin and atrazine. The preparation of organoclays was initially conducted by (i) the use of different types of non functionalised QACs at different concentrations of the surfactants and (ii) investigation and comparison of the adsorptive properties of three different organoclays, dodecyltrimethylammonium-, hexadecyltrimethylammonium-, and didodecyldimethylammonium-exchanged montmorillonites. The objective of this work was to determine the optimal conditions for the removal of the herbicides from water under different conditions (e.g. agitation time, pH, and different concentrations of herbicides) and evaluate the mechanisms involved in the adsorption process of herbicides.

2. Experimental methods

2.1. Materials

Pure Na-montmorillonite (referred as MMT) was purchased from Sigma–Aldrich and was used without purification. Based on the product specification, its cation exchange capacity (CEC) is 76.4 meq/100 g. Three different types of cationic surfactants were purchased from Sigma–Aldrich: (i) dodecyltrimethylammonium bromide (denoted as DDTMA, $C_{15}H_{34}NBr$, FW:308.34), (ii) hexadecyltrimethylammonium bromide (denoted as HDTMA, $C_{19}H_{42}NBr$, FW:364.46), and didodecyldimethylammonium bromide (denoted as DDDMA, $C_{26}H_{56}NBr$, FW:462.65).

2.2. Synthesis and characterisation of organoclays

The organoclays prepared are described in detail in a previously published paper by Park et al. [23,24] and were characterised by various techniques including X-ray diffraction (XRD), surface area measurement (BET method), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA). Their structural properties and characteristics were described by the previous work [23,24].

2.3. Batch adsorption of herbicides

Two different types of herbicides, imazaquin (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid) and atrazine (6-chloro-*N*-ethyl-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] were purchased from Sigma–Aldrich. Both imazaquin and atrazine were initially prepared in methanol as a stock solution (100 mg/L) and further diluted in water for the appropriate concentrations (0.5–20 mg/L). 0.1–0.2 g of the organoclays were placed in sealed 50 mL centrifuge tubes with 40 mL of imazaquin and/or atrazine solution in the appropriate concentration. The tubes were placed in a rotary shaker or a shaking water bath for 12 h at the appropriate temperature at 25 and 35 °C. The initial pH of imazaquin and atrazine was about pH 5 and 5.5. The mixture was filtered through PTFE 0.22 μm filters and the supernatants were analysed by a UV–Vis spectrometer (Agilent Cary 50) at 240 and 220 nm for imazaquin and atrazine, respectively, and a high-performance liquid chromatography (HPLC, Agilent HP 1100). The following conditions for the HPLC were used: 60:40 acetonitrile/water eluent mixture at a flow rate of 1 mL/min, a Luna 5 μ C18 column (Phenomenex Pty Ltd), 100 μL injection volume, and UV detection at 240 and 220 nm, respectively. To conduct the kinetic study (from 10 to 240 min), the adsorbents were added with an initial herbicides concentration (5 mg/L) at room temperature in determination of the equilibrium concentration. To evaluate the effect of pH on the adsorption of BPA (5 mg/L as an initial concentration of herbicides), the final pH of herbicides solutions was adjusted by either diluted 0.1 M HCl or NaOH. The quantity (q_e) of the adsorbed solutions was calculated [23,24].

3. Results and discussion

3.1. Adsorption of imazaquin and atrazine from single-component solutions

The fully characterised organoclays were used to evaluate their adsorption capacities for the removal of imazaquin and atrazine from aqueous solutions. Generally, the low adsorption of the herbicides onto hydrophilic MMT was observed and the adsorption results (in Fig. 2) demonstrated that the organoclays can remove 93.1% and 47.1% of imazaquin and atrazine, respectively.

It was found that organoclays were highly effective for the removal of imazaquin, but their efficiency in the adsorption of atrazine was relatively low. The results also showed that the amount of adsorbed herbicides was influenced by the size of surfactants as well as the saturation of organic cations. A similar finding from the investigation [25] reported the importance of the organic cations. Introduction of larger organic cations into the interlayer space of MMT has been attributed to an increase in basal spacing, which resulted in higher adsorption of herbicides. This study also demonstrated the packing density with an increase in surfactant loadings affected the adsorption of herbicides, but this factor may not be significantly affected in the current study.

Given the initial adsorption by organoclays intercalated with the different types of surfactants, the kinetic study of herbicide adsorption using organoclays was conducted (see Fig. 3). It appears that the amounts of imazaquin and atrazine adsorbed by the orga-