



Research paper

Modified halloysite as an adsorbent for prometryn from aqueous solutions



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ABSTRACT

Adsorption behavior of prometryn (2,4-bis (isopropylamino)-6-methylthio-s-triazine) on halloysite minerals has been studied in order to consider the application of such adsorbents in water purification. Halloysite, activated in various ways, was characterized by ASAP, SEM/EDS. Batch mode and flow system have been employed, using prometryn aqueous solutions. Various parameters were studied for both systems. Adsorption capacity was determined as a function of adsorbate concentration, of optimum contact time, optimum dose and adsorbent fragmentation. It was found that at pH = 5 the best adsorptive properties for prometryn are obtained for halloysite treated with 96% H₂SO₄. Such adsorption matches Langmuir and Freundlich models and is in a good agreement with pseudo-second order kinetic model. The desorption of prometryn from halloysite was also studied. The performed studies show that halloysite treated with 96% H₂SO₄ holds the great potential for removal of water impurities such as prometryn.

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1. Introduction

Herbicides, widely used in agriculture, are a serious problem as they are a potential source of environmental pollution, e.g., surface water, groundwater, precipitation (Scribner et al., 2005), as well as deposits in sediments, soil and biota.

Prometryn (Pr), a herbicide belonging to the group of s-triazines is a nonionic, weakly polar, and hydrophobic (log K_{ow} > 2) (Plakas and Karabelas, 2009) compound, with average solubility in water. It is stable at slightly acidic, slightly alkaline, and neutral environment (United States Environmental Protection Agency Office of Prevention, 1996). Its half-life is 270 days (Herbicide Handbook, 1994). For the first time Pr was registered as a plant protection product in 1964 in the United States by Ciba Crop Protection (United States Environmental Protection Agency Office of Prevention, 1996). It can be found in such products as Prometryn, Caparol, Gesagard, Primatol Q, and Prometex. They were widely used to control weeds, animal food, vegetables (celery, dill, parsley, and parsnips) and other crops (cotton and crops grown for seeds such as carrots, parsley, parsnip and coriander) (United States Environmental Protection Agency Office of Prevention, 1996).

In the European Union, Pr was withdrawn from use because of the potential risk to the environment and to the life and health of humans

as well as animals. In humans, for example, Pr can cause inhibition of thyroid hormone synthesis (Zapór, 2007). However, it is generally available outside the EU, for example in China, and sold as Prometryn and Pendimethalin. Accordingly, it may still be present in the soil and in all kinds of water circulating in nature.

There are many research programs aimed at reducing the impact of pesticides on water intended for human consumption. Attempts have been made of their disposal using different methods: physical – through infiltration (Krutz et al., 2003; Peña et al., 2011), coagulation (Brillas et al., 2003; Hladik et al., 2005), biological – for phytoremediation (Chuluun et al., 2009), culture macrophytes (Beketov and Liess, 2008; Matby et al., 2009; Brogan and Relyea, 2013), and the use of biotechnological methods (Hladik et al., 2005; Kanissery and Sims, 2011; Nawaz et al., 2011). For many years, the studies on the use of adsorbents for the removal of various herbicides from water have been conducted. Common adsorbents in such methods are carbon activated in different ways (Tae-Young et al., 2005; Chingombe et al., 2006; Derylo-Marczewska et al., 2010; Gupta et al., 2011; Hotton et al., 2011; Moreno-Castilla et al., 2011) and nanotubes (Pyrzyska et al., 2007; Paul et al., 2011a; Pyrzyska, 2011). Adsorption of pesticides was also studied on zeolites (Senthilkumaar et al., 2010; Yonli et al., 2012), montmorillonites (Chang et al., 2005; Akçay et al., 2006; Bansal, 2009; Park et al., 2011), sepiolites (Cardoso and Valim, 2006), and silica gels (Prado and Airoldi, 2001; Prado et al., 2004; Akçay et al., 2005; Kovaos et al., 2011; Paul et al., 2011b; Koner et al., 2012). The effectiveness of pesticide adsorption is affected by their solubility:

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organophosphorus pesticides (more soluble) are more difficult to remove than organochlorine ones (sparingly soluble) (Paul et al., 2011b). Another factor reducing the adsorption can be humic acids present in the purified water. On the one hand, they act as competitive adsorbates, while on the other hand they form hardly adsorbable hydrophilic complexes with eliminated pollutions.

The novelty of the present research is the application of the clay mineral – halloysite (Hal) for removing pesticides from water. Hal is defined as the hydrated kaolinite phase with monoclinic symmetry (Kohyama et al., 1978). Its structure is also described in the hexagonal system (Bayliss, 1989; Singh, 1996; Brigatti et al., 2006). The crystal structure consists of scrolled layers composed of a sheet of corner-sharing SiO_4 tetrahedral bonded to a sheet of edge-sharing AlO_6 octahedral to form a 1:1 layer silicate (Putnis, 1992; Yuan et al., 2012). The crystallographic water molecules and kaolinite OH groups are situated in the gap between the aluminosilicate layers. The layers have a tendency to roll into nanotubes to correct the lateral misfit between the silicate and aluminate sheets. A typical Hal tube is multi-walled; most tubes consist of more than ten layers. On average, Hal nanotubes have outer diameters of 50–100 nm and length values of around 1 μm (Yelleswarapu et al., 2010; White et al., 2012). This unique tubular structure of Hal in nano-scale and its many physico-chemical properties as a high surface area (60–500 m^2/g , depending on the modification process), porosity, large adsorption capacity, high susceptibility to ion exchange, and high chemical resistance over a wide pH range (Szeja et al., 2007). Its physicochemical properties suggest that it can make Hal a good adsorbent of water pollution, including herbicides (Zhao et al., 2013). Hal has also attracted most interest for new technology applications. Hal nanotubes (HNT) are a potential substitute for other synthetic less environmentally-friendly, and expensive nanotubes, such as carbon nanotubes (CNT) (Du et al., 2010).

Industrial applications of such minerals as Hal depend on their surface properties. Several methods have been suggested to improve surface properties by including mechanochemical activation (Tang et al., 2010), intercalation (Mellouk et al., 2009; Cheng et al., 2011), and chemical activation (Tang et al., 2010). The example of the last method is an acid treatment which causes disaggregation of clay particles, the elimination of mineral impurities, and the dissolution of the external layers. As a result, surface area, surface activity, and pore volumes increase (Lenarda et al., 2007; Panda et al., 2010; Zhang et al., 2012; Banaś et al., 2013; Szczepanik et al., 2015). A high level of biocompatibility and low cytotoxicity of Hal made this material and its modifications also as a potential carrier for loading various drug molecules (Price et al., 2001; Levis and Deasy, 2003; Kelly et al., 2004; Veerabadran et al., 2007; Forsgren et al., 2010; Shi et al., 2011; Vergaro et al., 2012; Tan et al., 2013; Tan et al., 2014).

This paper presents the results of studies on Pr adsorption from an aqueous solution on Hal and its desorption. Studies were conducted both in batch and flow systems. The effect of various factors such as the Hal modification method, its fragmentation, the optimum contact time between the adsorbent and the adsorbate, the optimal mass of Hal, Pr optimal dose on a particular mass of adsorbent and the solution pH is presented.

2. Material and methods

2.1. Characteristics

The chemical composition of Hal was earlier measured by X-ray fluorescence (XRF) (Banaś et al., 2013). The nitrogen adsorption isotherm was measured at 77 K via ASAP 2020 instrument (Micrometrics, Norcross, Ga, USA), using nitrogen with 99.99% purity. Hal was firstly outgassed at 537 K for at least 6 h in vacuum. The specific surface area was determined using adsorption data by applying the Brunauer–Emmett–Teller (BET) equation. The FEI QUANTA 250 Scanning Electron

Microscope with the EDS microanalyser and digital image recorder was used to obtain information on quality concerning morphology and elementary composition of a sample as well as information on quantity concerning concentration of particular elements in a sample during one analysis stage. Absorption spectra were recorded on the Shimadzu UV 3600 spectrophotometer.

Certified analytical standard of Pr ($99.7 \pm 0.1\%$) was purchased from the Institute of Industrial Organic Chemistry (Annopol, Poland). Hal was obtained from the strip mine “Dunino” located in Lower Silesia, near Legnica, Poland. The study used coarsely granular Hal ($\phi > 1.0 \text{ mm}$) and fine-grained one with diameters included in the ranges: 0.6–0.4 mm 0.4–0.25 mm, 0.25–0.12 mm.

Hal was modified with 96% H_2SO_4 (analytical grade, POCH Gliwice)–ASHal, 65% HNO_3 (analytical grade, POCH Gliwice)–ANHal, and 30% NaOH (p.a., Chempur Warszawa)–BHal: to each 10 g of the mineral the above mentioned solutions (200 cm^3) were respectively added. After 2 h, the Hal was rinsed out until the water above Hal stopped absorbing electromagnetic radiation at the wavelength of 222.0 nm.

2.2. Adsorption procedure

The determination of the Pr adsorption on Hal was based on changes in its concentration in the aqueous solution after the contact with the adsorbent. This concentration was determined by spectrophotometry, based on the calibration curve. Absorbance measurements were performed in the spectral range 190–350 nm, in quartz cuvettes with a thickness of 1 cm.

The degree of adsorption (α) was calculated from the following equation (Jamil et al., 2011):

$$\alpha = \frac{A_0 - A}{A_0} \cdot 100\% \quad (1)$$

where A_0 and A are the Pr solution absorbance before and after contact with Hal, respectively.

Studies in the batch system were carried out at $25 \pm 0.1^\circ\text{C}$. Pr solution was used at a concentration of $C = 2.15 \cdot 10^{-5} \text{ mol/dm}^3$ and sample masses of Hal were properly prepared. Due to the strong hydrophilic properties of the mineral, the dried sample was conditioned prior to use by distilled water of a volume of 10 cm^3 . After 24 h, 8 cm^3 of water was taken from the system and 8 cm^3 of the Pr solution was added. The remaining volume of distilled water in the system (2 cm^3) was included in the calculations of Pr concentration in the solution.

The optimum contact time of the herbicide with the adsorbent was determined by measuring of the solutions absorbance after a given time: 5, 10, 15, 30, 60, 240 min and 24, 48, and 72 h.

In order to determine the optimal Hal mass on which the maximum amount of Pr will be adsorbed, the samples of the adsorbent with masses of 0.1–2.0 g were prepared. To each sample of Hal 8 cm^3 of Pr was added, the system was mixed and allowed to stand for 24 h. Then the absorbance of these Pr solutions was measured.

The effect of the herbicide concentration on its adsorption on Hal was tested by adding 5 cm^3 of Pr solution with various concentrations to 0.1-g Hal mass. After 72 h, the absorbance of Pr in each solution was measured.

In order to investigate the effect of pH on the adsorption, the absorption spectra of Pr solutions at pH = 1, 3, 5, 7, 9, 11, and 13, prepared with HCl and NaOH were recorded. 8 cm^3 solution of Pr with an appropriate pH was added to the Hal and left for 48 h, and then the absorbance was measured.

In order to investigate the desorption of Pr from Hal, Hal saturated with Pr was prepared: to 10 g of Hal was added 100 cm^3 of Pr solution at concentration $C = 8.7 \cdot 10^{-5} \text{ mol/dm}^3$, after 10 days the solution of Hal was decanted. In order to determine equilibrium concentration,

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