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Adsorption of chloroanilines from aqueous solutions on the modified halloysite



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ABSTRACT

Batch removal of 3-, 4-chloroaniline and 3,4-dichloroaniline from an aqueous solution using unmodified and acid-activated halloysite was investigated in this study. The influence of acid concentration used for digesting the halloysite, contact time as well as the concentration of chloroaniline solutions was reported.

The results show that the adsorption of 4-chloroaniline was greatly enhanced by using a sulfuric acid-treated halloysite, as compared to the unmodified halloysite. A comparison of kinetic models applied to the adsorption of chloroanilines on an acid-treated halloysite was evaluated for pseudo first-order, pseudo second-order, and intraparticle diffusion kinetic models. The chemisorption pseudo-second order kinetic model was found to correlate the experimental data well. The adsorption mechanism of acid-treated halloysite-chloroaniline system complied well with the Langmuir model in the case of 4-chloroaniline and 3,4-dichloroaniline and with the Freundlich model for 3-chloroaniline.

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1. Introduction

Mono- and dichloroanilines are important reagents or chemical intermediates in the production of polymers, rubber additives, dyes, pharmaceuticals, and agricultural agents. They are produced in biodegradation processes of phenylurea, and phenylcarbamate herbicides (Gosetti et al., 2010; Loos et al., 2003; Norberg et al., 1997; Othmen and Boule, 1999). Chloroanilines are toxic compounds with large diffusion, high persistence and accumulation as well as low natural biodegradability. In recent years, the remediation strategies have been developed for destructing these compounds, based on different processes and reagents (Augugliaro et al., 2000; Chu et al., 2007; Coppo et al., 2001; David et al., 1998; Emtiazi et al., 2001; Evgen'ev et al., 2003; Hofmann et al., 2005; Sanchez et al., 2002). Wastewaters are traditionally treated with photodecomposition (Chu et al., 2007; Coppo et al., 2001; David et al., 1998), electrolysis (Kadar et al., 1999, 2001), oxidation (Gomes et al., 2005; Jagtap and Ramaswamy, 2006), adsorption (Angioi et al., 2005; Kowalska and Cocke, 1998), biodegradation (Tongarun et al., 2008), and other processes. Generally, adsorption technology has proved to be one of the most effective techniques in the separation and removal of a wide variety of organic pollutants from wastewaters (Pavlovic et al., 2005; Ulibarri et al., 1995). Several adsorbents have been used for the treatment of effluents containing chloroanilines, for example activated carbon (Laszlo, 2005), chemical

modified polymeric matrix (Cai et al., 2005), or other low-cost adsorbents (Andini et al., 2008). The adsorption of mono-, di- and trichloroanilines on kaolinite and Na-montmorillonite was studied by Angioi et al. (2005). The authors proved a higher adsorption ability of Na-montmorillonite with respect to kaolinite. Halloysite (Hal) is a 1:1 layered clay mineral with one silica tetrahedron sheet and one alumina octahedron sheet (Brigatti et al., 2006). Due to its unique tubular structure in nano-scale and many physico-chemical properties (such as good mechanical properties, excellent chemical stability, high specific surface area and porosity, and large adsorption capacity), Hal is a potential cheap alternative to expensive carbon nanotubes (Dong et al., 2012). Acid treatment is one of the most common chemical modifications of clay minerals (Frini-Srasra and Srasra, 2008). Hydrochloric and sulfuric acids are probably among those most widely used in acid activation, because they show strong affection to an increase of specific surface area, porosity, and adsorption capacity (Zhang et al., 2012).

In this paper, the adsorption of 3-chloro-, 4-chloro-, and 3,4-dichloroaniline from an aqueous solution on unmodified and chemically modified Hal was studied in the batch system.

2. Material and methods

2.1. Chemicals

Hal was obtained from the strip mine "Dunino" (Intermark Company, Legnica, Poland). 3-Chloroaniline (3CA), 4-chloroaniline (4CA) and 3,4-dichloroaniline (34DCA) were purchased from Aldrich. Sulfuric acid

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Table 1

Concentrations of the elements in halloysite (Hal) samples activated with different concentrations of H₂SO₄ measured by using the WDXRF method (Banaś et al., 2013).

Element (%)	Acid concentration (mass%)					Error (%)
	10%	20%	40%	50%	65%	
Al	18.3	17.6	16.9	13.6	16.7	~10
Si	20.4	19.0	19.8	22.9	19.3	~10
O	42.1	42.4	47.8	52.5	47.9	~5
Fe	16.3	17.7	12.6	8.24	13.3	~10

(VI) was purchased from P.O.Ch. Gliwice (Poland). All the reagents were analytical grade chemicals.

2.2. Preparation of adsorbent

Hal was sieved through a sieve with a 0.25 mm diameter and washed with distilled water to remove residual contamination from mining. In order to activate Hal, the weighed 250 g samples were treated with 10, 15, 20, 40, 50, and 60 mass% H₂SO₄. The samples were stirred at temperatures ranging from 40 to 50 °C for 60 min. Then the solution was decanted and samples were washed with distilled water to obtain pH value of water of about 5. Finally, Hal was dried at about 100 °C for 24 h. The final product was labeled as acid-treated Hal (AHal). The procedure was repeated three times to obtain the adsorbent having reproducible properties.

2.3. Characterization of halloysite

The analysis of Hal was performed using wavelength dispersive X-ray fluorescence analysis (WDXRF) (an AXIOS spectrometer from PANalytical equipped with an X-ray tube (Rh anode) with a maximum power of 2.4 kW and X-ray exit windows placed at 45° just in the front of the sample holder) (Banaś et al., 2013).

Nitrogen adsorption isotherms were measured at –196 °C on an ASAP 2020 volumetric analyzer manufactured by Micromeritics, Inc. (Norcross, GA, USA). All samples were outgassed at 350 °C for 6 h prior to adsorption measurements. The BET (Brunauer–Emmett–Teller) specific surface area S_{BET} was calculated from nitrogen adsorption isotherms in the range of relative pressures from 0.05 to 0.3 using the cross-sectional area of 0.162 nm² per nitrogen molecule. The single-point total pore volume of pores (V_t) was estimated from the volume adsorbed at a relative pressure of $p/p_0 = 0.3$. The adsorption average pore width and the BJH adsorption average pore diameter (Barrett–Joyner–Halenda Pore Size and Volume Analysis) were used for characterization of the raw and modified Hal samples studied.

2.4. Batch adsorption experiments

Batch adsorption experiments were conducted in a 100 ml Erlenmeyer flask containing 2 g of adsorbent and 50 ml ultrapure water from the Milli Pore system. The flask was shaken in a shaker at 120 rpm for 24 h to wet the adsorbent. Then water was decanted and 20 ml of the investigated chloroaniline solution was added. The concentrations of amine solutions were in the range from 5 mg/l to 80 mg/l. The flask was agitated at 120 rpm and room temperature for 24 h in a rotary shaker to ensure adsorption equilibrium. After that the solution was decanted and filtered to collect the supernatant. The residual chloroaniline concentration in the

supernatant was determined using a UV–VIS–NIR UV-3600 Shimadzu spectrophotometer. Hal samples after adsorption were dried and the procedure was repeated with 20 ml of water to obtain the concentration of amine after the desorption process.

The removal efficiency, R (%) and the amount of chloroaniline adsorbed at equilibrium (adsorbate uptake, q_e , mg/g) were calculated by using the following equations:

$$R = \left(\frac{C_o - C_e}{C_o} \right) \cdot 100\% \quad (1)$$

where: C_o and C_e (mg/l) are the initial and equilibrium concentrations of chloroaniline solutions.

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

where: C_o and C_e (mg/l) are the initial and equilibrium concentrations of chloroaniline solutions, V (l) is the volume of the chloroaniline solution, and m (g) is the dosage of Hal and AHal samples.

3. Results and discussion

3.1. Characterization of halloysite

The results of the element analysis of Hal activated by sulfuric acid (VI) (AHal) in the range of concentration 10–65 mass% obtained by the WDXRF method are collected in Table 1 (Banaś et al., 2013). The amount of Al and Fe decreases with the increase of H₂SO₄ concentration up to 50%, particularly in the case of Fe.

Structural parameters calculated from adsorption isotherms were as follows: specific surface area (S_{BET} , m²/g) is equal to 43.141 m²/g and 76,601 m²/g, and total pore volume (V_t , cm³/g) is equal to 0.021 and 0.039 for Hal and AHal, respectively (Table 2). Acid digestion results in almost twice the increase in the value of the specific surface area and a total pore volume for Hal.

3.2. Batch adsorption studies

The effect of H₂SO₄ concentration used for the modification of Hal on the removal of the chloroanilines investigated from an aqueous solution was studied over the range of acid concentration from 20 to 65 mass%. The obtained results for AHal and for comparison for raw Hal are shown in Fig. 1. An increase of acid concentration increased the removal of 4CA, 3CA and 34DCA up to 50% H₂SO₄. The adsorption of the chloroanilines is the strongest on Hal modified by 50% sulfuric acid. Further increase of acid concentration causes the decrease of removal efficiency of the chloroanilines. The desorption of the adsorbed 4CA, 3CA and 34DCA on Hal is the smallest in the range of acid concentration from 50 to 65 mass% only for 4CA (Fig. 1). Studies of the influence of acid concentration on Hal modification were carried out in order to select optimal conditions of this process. The adsorbent modified by 50% acid (AHal) was chosen for further investigation of the adsorption of 4CA and other studied chloroanilines on Hal.

3.2.1. Effect of contact time

Batch adsorption experiments were conducted at room temperature and pH about 5 at different time intervals in order to determine the optimum contact time. The predetermined time intervals were 10, 20,

Table 2

Characteristics of unmodified (Hal) and acid activated samples of the halloysite (AHal) used in the experiments.

Halloysite	Specific surface area S_{BET} , m ² /g	Total pore volume V_t , cm ³ /g	Average pore diameter w_i , nm	Average pore width w_e , nm
Unmodified (Hal)	43.141	0.021	2.04	1.99
Acid treatment (50% H ₂ SO ₄) (AHal)	76.601	0.039	2.05	2.02

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