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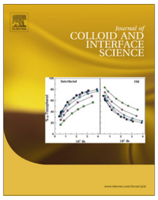

Halloysite nanotubule clay for efficient water purification

Yafei Zhao[a], Elshad Abdullayev[a], Alexandre Vasiliev[b], Yuri Lvov[a,*]

[a] *Institute for Micromanufacturing, Louisiana Tech University, 911 Hergot Avenue, Ruston, LA 71272, United States*
[b] *Physics Department, M. Lomonosov Moscow State University, Leninskie Gory, Moscow 119991, Russia*

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ABSTRACT

Halloysite clay has chemical structure similar to kaolinite but it is rolled in tubes with diameter of 50 nm and length of ca. 1000 nm. Halloysite exhibits higher adsorption capacity for both cationic and anionic dyes because it has negative SiO_2 outermost and positive Al_2O_3 inner lumen surface; therefore, these clay nanotubes have efficient bivalent adsorbancy. An adsorption study using cationic Rhodamine 6G and anionic Chrome azurol S has shown approximately two times better dye removal for halloysite as compared to kaolin. Halloysite filters have been effectively regenerated up to 50 times by burning the adsorbed dyes. Overall removal efficiency of anionic Chrome azurol S exceeded 99.9% for 5th regeneration cycle of halloysite. Chrome azurol S adsorption capacity decreases with the increase of ionic strength, temperature and pH. For cationic Rhodamine 6G, higher ionic strength, temperature and initial solution concentration were favorable to enhanced adsorption with optimal pH 8. The equilibrium adsorption data were described by Langmuir and Freundlich isotherms.

1. Introduction

Dyes and pigments from textiles, printing, paper, plastics, leather and pulp productions are often toxic and environmentally unsafe, and discharge of colored effluents from these industries wastewater is needed [1,2]. Precipitation, coagulation, membrane separation, photo-degradation, ion exchange and adsorption have been extensively exploited for dyes-contaminated wastewater treatment [3–6]. Among them, adsorption has received increasing attention due to high efficiency, environmental friendliness, low cost, easy operation, insensitivity to toxic substances and the possibility of the materials recycling. Many low-cost mesoporous adsorbents have been tested including zeolites, kaolinite and montmorillonite clays, banana peel, saw dust, fly ash, and other materials [1,4,7–11]. However, none of the above materials show high adsorption capacity for both positive and negative dyes.

Recently, halloysite nanotubes, economically viable clay mineral, attracted a great interest due to their hollow tubular structure, high surface area and unique surface properties. Halloysite is a naturally occurring 1:1 dioctahedral aluminosilicate clay mineral chemically similar to kaolinite. A comparative study on structure and morphology of halloysites from six different natural deposits have been presented in a recent paper and their potential as nanoadsorbents, fillers in polymer composites and containers for loading active agents was demonstrated [12]. Halloysite nanotubes with ca. 50 nm diameter, 10 nm lumen and 1 μm length are formed by rolling kaolinite sheets during natural hydrothermal process [13–18]. Halloysite tubes have multilayer walls with negatively charged Si–OH on the outer surface and positively charged Al–OH on the inner surface (at pH between 4 and 9) and does not require exfoliation, contrary to the kaolinite plate-like morphology. This unique bivalent morphology with spatially separated negative and positive surfaces makes halloysite tube a promising absorbent for variety of pollutants, both positive and negative [19–23].

The adsorption properties of halloysite with cationic dyes and heavy metal ions were reported, but anionic dye adsorption was not studied though it may be specifically controlled with its positively charged lumen. Halloysite can be modified by silane coupling agents, surfactants, metal complexes and polyelectrolytes for higher adsorption capacity [24–28]. We present here the halloysite adsorption study of cationic dye Rhodamine 6G and anionic dye Chrome azurol S and its comparison with kaolinite clay adsorption. Comparison of adsorption isotherms for two mesoporous materials with similar chemistry but different morphology (tubule and plate) was performed in dependence on adsorbent dose, pH, temperature and initial concentration. Halloysite surface was modified with surfactants and polyelectrolytes to reveal the major forces involved in adsorption process.

2. Experimental and methods

2.1. Materials

Halloysite from Applied Minerals Inc. (USA) was used without further treatment. Kaolinite was purchased from Sigma (USA)

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* Corresponding author.
E-mail address: ylvov@latech.edu (Y. Lvov).

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and used without pretreatment. Analytical reagent grade Rhodamine 6G ($C_{28}H_{31}N_2O_3Cl$) and Chrome azurol S ($C_{23}H_{16}C_{l2}O_9S{\cdot}3Na$) were purchased from Sigma–Aldrich Chemicals. Other chemicals used are poly(ethyleneimine) (PEI), poly(4-styrenesulfonic acid) (PSS), hexadecyltrimethyl ammonium bromide (HDTMA), poly(diallyldimethyl ammonium chloride) (PDDA), sodium dodecylsulfate (SDS) and dioctadecyldimethyl ammonium bromide (DODAB), hydrochloric acid (HCl), sodium hydroxide solutions (NaOH) and sodium chloride (NaCl), all analytical grade reagents.

Stock solutions (1000 mg/L) were prepared by dissolving Rhodamine 6G and Chrome azurol S in deionized water. One molar solutions of HCl, NaOH and NaCl were used for pH and ionic strength adjustments.

2.2. Characterization

Fourier transformed infrared spectroscopy was performed with Nicolet Nexus 470 FTIR spectrometer using KBr pellets in the range of 400–4000 cm^{-1} to observe clay surface functional groups. Field emission scanning electron microscopy was done with Hitachi S-4800 FE-SEM, operating at secondary electron imaging mode at 1–3 kV. Transmission electron micrographs (TEMs) were obtained with a Zeiss EM 912 microscope equipped with a CCD camera operating at120 kV. Nitrogen adsorption–desorption isotherms were measured with NOVA 2200, Quanto Chrome Instruments at 77 K for the specific surface area estimations with the BET (Brunauer Emmett Teller) technique. Thermogravimetrical analysis (TGA) was carried out using Q50 Thermal Analyzer (TA Instruments) at 25–600 °C range in N_2 atmosphere. Samples were heated at 10 °C/min rate. The electrical surface ζ-potential of microparticles was measured at room temperature with Brookhaven Zeta Plus analyzer.

2.3. Dyes adsorption experiments

The batch experiments were carried out in 2 mL centrifuge tubes containing 1 mL of dye solutions and 2 mg adsorbent clay (except for the study of the adsorbent dose effect on dye adsorption, in which amount of clay indicated within the context). The tubes were left at 20–60 °C to reach equilibrium on dye adsorption. Then tubes were centrifuged for 5 min at 14,000 rpm and the concentration of supernatant was determined using UV–Vis Spectrophotometer (Agilent, 8453). The removal efficiency (R, %) and the amount of dyes adsorbed at equilibrium (q_e, mg/g) were calculated by using the following equations:

$$R = \frac{100(C_0 - C_e)}{C_0} \tag{1a}$$

$$q_e = \frac{1000(C_0 - C_e)V}{M} \tag{1b}$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of dyes solution; V (L) is the volume of dyes solution and M (mg) is the weight of adsorbents. Strong UV adsorption of dyes allows determination of their concentration at ranges down to ppm levels and hence provides very precise determination of the removal efficiency (up to three decimal points).

2.4. Water filters and regeneration study

The water filter system was set up as in Fig. 2. One gram of adsorbent clay was added to the water filter and cellucotton was used to block the adsorbent powder. The system was kept at 20 °C. 300 mg/L Rhodamine 6G and Chrome azurol S dyes solution were studied in the system and dyes concentration were determined after filtration, respectively.

In order to study the reusability of halloysite, the used adsorbents were dried under 60 °C in the oven and burned at 300 °C. After that, the burned samples were reused as adsorbents in the water filter system and dyes concentration were measured again after filtration. The adsorption-burning-adsorption cycle were repeated for five times.

2.5. Adsorption isotherms

Both Langmuir and Freundlich models were used for the fitting experimental data. The linear form of Langmuir equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{2}$$

where q_e (mg/g) is the equilibrium amount of dyes adsorption by halloysite or kaolinite, C_e (mg/L) is the equilibrium dyes concentration in the solution, q_m (mg/g) is the maximum adsorption of dyes and K_L (L/mg) is the Langmuir constant related to the enthalpy of the process. q_m and K_L can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e, respectively. The dimensionless constant separation factor (R_L) can be used to evaluate whether the adsorption process is favorable or unfavorable, which is calculated using

$$R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

where K_L is the Langmuir constant and C_0 is the initial concentration of dyes. It represents favorable adsorption process when $0 < R_L < 1$; unfavorable adsorption if $R_L > 1$; linear adsorption when $R_L = 1$; and irreversible adsorption in the case of $R_L = 0$.

The linear form of Freundlich equation can be written as:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{4}$$

where K_F (mg/g $(mg/L)^{1/n}$) and n is Freundlich constant related to the adsorption capacity and intensity, C_e (mg/L) is the equilibrium dyes concentration. K_F and $1/n$ can be calculated by plotting $\log q_e$ versus $\log C_e$. Higher value for K_F reflects higher affinity for dyes and it indicates favorable adsorption when $0.1 < 1/n < 1$, whereas unfavorable adsorption takes place when $1/n > 1$ [29].

3. Results and discussion

3.1. Structural properties and surface chemistry of halloysite and kaolinite

Both the textural properties and the surface chemistry affect the adsorption behavior of an adsorbent and comparative study of halloysite and kaolinite allows to their specification. Halloysite formed of rolled alumosilicate sheets with an ideal formula of $Al_2Si_2O_5(OH)_4 \times nH_2O$, and it is similar to kaolinite with additional water between the adjacent layers. When raw halloysite is mined from deposits, it has hydrated form with $n = 2$, and after drying at elevated temperature it irreversibly loses water transforming into more common product called halloysite – 7 Å (indicating its interlayer d_{001}-spacing) or just halloysite [12–15]. SEM and XRD analysis showed that the halloysite sample is comprised of over 99% of tubes with minor amounts of quartz as impurity. Elemental composition was as follows:46.1% SiO_2, 38.7% Al_2O_3, 0.2% CaO, 0.1% Fe_2O_3 and 14.6% loss on ignition.

Halloysite has a cylindrical shape with hollow open-ended lumen of 0.5–1 μm length (Fig. 3a–c). Multilayer tubule wall is comprised of 15–20 aluminosilicate sheets packed with 0.72 nm spacing. The inner and outer diameter of halloysite is in the range 10–20 nm and 40–60 nm, while the wall thickness is 15–20 nm.