Nanotubular Halloysite Clay as Efficient Water Filtration System for Removal of Cationic and Anionic Dyes

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Abstract. Halloysite nanotubes, chemically similar to kaolinite, are formed by rolling of kaolinite layers in tubes with diameter of 50 nm and length of ca. 1 µm. Halloysite has negative SiO$_2$ outermost and positive Al$_2$O$_3$ inner lumen surface, which enables it to be used as potential absorbent for both cationic and anionic dyes due to the 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 kaolinite. 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. These results indicate a potential to utilize halloysite for the removal of ionic dyes from environmental waters.

1. Introduction

Synthetic dyes are widely used in leather, paper, textile, etc. Discharge them into waters causes environmental various problems due to their carcinogenicity, toxicity to aquatic life and undesirable aesthetic aspect [1, 2]. Various methods including precipitation, coagulation, membrane separation, photo-degradation, ion exchange and adsorption have been extensively exploited for dyes-contaminated wastewater treatment [3-6]. Adsorption has been proved to be a highly efficient and relatively low-cost technique for the treatment of dye contaminated waters due to high efficiency, environmental friendliness, low cost, easy operation, insensitivity to toxic substances and the possibility of the materials recycling. Generally, zeolites, kaolinite and montmorillonite clays, banana peel, saw dust, fly ash, and other materials [1, 4, 7-11] have the disadvantages of high costs and resulting problems associated with their subsequent treatment and regeneration. Most important of all, none of these materials has high adsorption capacity for both positive and negative dyes.

Halloysite is a two-layered aluminosilicate clay mineral, consisting of one alumina octahedron sheet and one silica tetrahedron sheet in 1:1 stoichiometric ratio, which is available in abundance in China as well as other locations around the world. 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 don’t 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 a variety of pollutants, both positive and negative [19-23]. Literature has studied the adsorption properties of halloysite with cationic dyes and heavy metal ions, 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].

In this paper, we investigate 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
Halloysite from Applied Minerals Inc (USA) was used without further treatment. Kaolinite was purchased from Sigma (USA) and used without pretreatment. 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 14000 rpm and the concentration of supernatant was determined using UV-Vis Spectrophotometer (Agilent, 8453). For the water filter system, 1 g 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.

3. Results and Discussion
3.1. Morphology characterization of halloysite and kaolinite
SEM is used to observe the morphological structures of HNTs and kaolinite. It can be seen from Figure 1a and 1b that HNTs has a cylindrical shape with 15-20 aluminosilicate layers rolled in the multilayer tubule walls with a layer spacing of 0.72 nm. It has hollow and open-ended lumen with a length of 0.5-1 mm. The inner and outer diameter of HNTs is in the range 20-30 nm and 40-50 nm, while the wall thickness is 15-20 nm. kaolinite has a base shape and lamellar structure. The particle size of kaolinite is estimated 1-15 µm.

![Figure 1. SEM images of halloysite nanotubes and kaolinite](image)
3.2. Adsorption properties of halloysite and kaolinite

Adsorption behaviors of positively charged dye -Rhodamine 6G and negatively charged dye - Chrome azurol S (Fig. 1) were studied with halloysite and kaolinite powders using aqueous dyes of 0 – 0.05wt%. The maximum adsorption capacity calculated from Langmuir model is 43.6 mg/g for Rhodamine 6G and 38.7 mg/g for Chrome azurol S onto halloysite, and 21.4 mg/g for Rhodamine 6G and 36.7 mg/g for Chrome azurol S onto kaolinite.

It can be observed that halloysite has better adsorption for both of the dyes as compared to kaolinite. The larger surface area of halloysite, gives more sites for dye adsorption. Besides, both negative outer surface and positive inner surface of the halloysite are exposed to the solution, allowing adsorption of both positive and negative molecules. Water filtration system and regeneration of halloysite and kaolinite

![Figure 2. Adsorption of Rhodamine 6G and Chrome azurol S onto halloysite and kaolinite (H-halloysite, K-kaolinite, RG-Rhodamine 6G, CS-Chrome azurol S).](image)

3.3. Water filter system and regeneration study

Water filters were prepared using halloysite and kaolinite clays (Figure 3). Filtration efficiency was tested by passing 30 mL of 300 mg/L dye solution. Chrome azurol S was completely removed from contaminated water by halloysite, as it is clearly evident from UV spectra of the filtered liquid samples. In spite of having similar chemical structure, kaolinite was shown to be poor filter. Probably this is associated with nanoporous structure of the halloysite. Small pores of ca. 5-10 nm diameter efficiently adsorb dyes from the solution before it passes from the filter. Similar tendency was observed for the case of Rhodamine 6G as well; over 99% of the dye was removed by the halloysite filter.

Dyes can be removed from adsorbed filters by burning at 300 °C. Second generation reusable filters were made and their efficiency was demonstrated using Chrome azurol S and Rhodamine 6G. Halloysite showed significantly better reusability compared to kaolinite. Filtrate from halloysite filters are almost completely transparent for both the dyes, indicating near filtration efficiency for both the negative and positive dyes. Their efficiency compares fairly well with the efficiency of first generation halloysite filters. With this we may conclude that halloysite almost completely preserved its dye removal efficiency after first reuse. On the other hand, significant amount of dye passed from kaolinite filters, indicating its poor filtration efficiency. Furthermore, halloysite filters have been effectively regenerated up to 5 times by burning the adsorbed dyes.
3.4. External factors affecting dye adsorption efficiency

Effect of initial concentration and temperature, adsorbent dose, pH and ionic strength onto HNTs were studied in detail and displayed in Figure 4. From Figure 4a, it shows the adsorption capacity increased with the increase of dyes concentration. This is due to higher concentration can provide higher driving force to overcome the resistance to the mass transfer of dyes between the aqueous and solid phases. Temperature also has important impact onto the adsorption process. The adsorption capacity of Rhodamine 6G onto HNTs was found to increase with increase in temperature while that of Chrome azurol S onto HNTs was decrease. These results indicate the adsorption process for Rhodamine 6G and Chrome azurol S is endothermic and exothermic, respectively. A possible mechanism of interaction is the reaction between the hydroxyl groups of HNTs and cationic/anionic group in the dye molecules. At initial pH 6, HNTs is negatively charged and thus such reaction is electrostatic attraction for cationic dyes and repulsion for anionic dyes. Either electrostatic attraction or repulsion effect could be enhanced at higher temperature. Thus, this results in the increase for Rhodamine 6G removal but the decrease for Chrome azurol S adsorption.

From Figure 4b, it was observed that the removal efficiency increased from 51.4% to 89.0% for Rhodamine 6G and from 43.9% to 72.8% for Chrome azurol S with an increase in adsorbent dose from 1 to 15 mg. This may be due to more adsorbent dose gives more surface area and thus results in more available adsorption sites.

It is well-known that pH is a crucial parameter because it strongly affects not only the surface charge of the adsorbent, the degree of ionization of the materials, the dissociation of functional groups on the active sites of the adsorbent, but also the structure of the dye molecule. Furthermore, it delineates the mechanism involved in adsorption process. Figure 4c illustrates dyes adsorption by HNTs as affected by pH from 3 to 12. The optimum pH for Rhodamine 6G is found to be around 8 and the adsorption capacity of Chrome azurol S decreases with the increase of pH. The reason for the strong dependence of adsorption capacity on pH can be explained that the surface charge of HNTs is significantly affected by solution pH. The pH$_{ZPC}$ of HNTs was found to be 2.75. The surface of HNTs is positively charged below pH 2.75, while it is negatively charged above 2.75. Besides, the zeta potential of HNTs is more negative with increase in pH in the range pH 3 to pH 12. The electrostatic interaction between the dye molecules and the adsorbent surfaces can be either attractive or repulsive, therefore the adsorption capacities should increase when the interactions are attractive and decrease when they are repulsive. With the increase in pH, either attraction or repulsion can increase. As discussed previously, Rhodamine 6G is a cationic dye and therefore experiences attraction with the negatively charged HNTs, while Chrome azurol S is an anionic dye and thus experiences repulsion with negative HNTs. Therefore, increasing electrostatic attraction between negatively charged adsorption sites and positively charged Rhodamine 6G causes an increase in Rhodamine 6G removal, whereas increasing electrostatic repulsion between negatively charged adsorption sites and negatively

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**Figure 3.** Photographs of the water filters prepared by one gram of halloysite and kaolinite clays, tested on 300 mg/L concentration Chrome azurol S (a), 300 mg/L concentration Rhodamine 6G (b) and mixture of these dyes 150 and 150 mg/L (c) solutions with 300 mg/L concentration.
charged Chrome azurol S results in a decrease in Chrome azurol S removal. On the other hand, the poor adsorption at lower pH (pH<8) may be due to the excessive H⁺ ions competing with Rhodamine 6G for adsorption sites. The adsorption for Rhodamine 6G decreases when pH above 8. This may be due to the deprotonation of the substance in alkaline solution (as one can see Rhodamine 6G (pKa=7.5) is a weak base and can easily lose its protons by the effect of strong bases, which leads to the partial neutralization of its positive charge. As a result, electrostatic interaction with negatively charged halloysite decreases and thus results in the decrease in the adsorption capacity.

Since industrial wastewater always contains various additives such as inorganic salts, it is necessary to investigate how these ions affect the adsorption behavior for dyes. 2 mg of HNTs were added into 1 mL of 100 mg/L dye solution with different NaCl concentration at room temperature. The results are depicted in Figure 4d. The adsorption capacities of Rhodamine 6G and Chrome azurol S on HNTs were significantly affected by the presence of NaCl. When NaCl concentration increased from 0 to 1 mol/L, the adsorption capacity of Rhodamine 6G by HNTs increased from 29.5 to 45.3 mg/g but the adsorption capacity of Chrome azurol S decreased from 20.4 to 8.3 mg/g. Ionic strength can influence zeta potential of HNTs. Zeta potential of HNTs is negative at natural condition and it becomes less negative when increase the concentration of NaCl. Accordingly, the electrostatic attraction effect between HNTs and Rhodamine 6G decreases whereas the electrostatic repulsion effect between HNTs and Chrome azurol S increases. Consequently, the adsorption capacity of HNTs for Rhodamine 6G decreases but for Chrome azurol S increases.

**Figure 4.** Effect of (a) temperature and concentration (b) adsorbent dose (c) pH (d) ionic strength

4. Conclusion

Natural halloysite nanoclay, an abundantly available tubule form of kaolin, was studied as an efficient adsorbent both for cationic and anionic aqueous dyes. Tubular morphology of halloysite favors dye removal, as compared with chemically similar platy kaolin multilayer stacks. The influence of temperature, pH, ionic strength and adsorbent amount of cationic Rhodamine 6G and anionic Chrome
azurol S revealed molecular details involved in the adsorption process. Ionic interaction is the major force in Rhodamine6G adsorption on halloysite, while hydrogen bonding was the most essential for Chrome azurol S adsorption.

Halloysite is novel nano-material which can be used in water filter system. The removal efficiency of halloysite is higher than most of conventional adsorbents. Besides, halloysite can be regenerated by burning after adsorption and be reused. Dye removal efficiency exceeded 99.9% after 5 reuse cycles for negative Chrome azurol S and 95% for positive Rhodamine 6G. Optimal pH for Rhodamine 6G adsorption was in the range of 8 and 9 while acidic solutions were favorable for Chrome azurol S adsorption. Higher temperatures favor Rhodamine 6G adsorption, indicating the endothermic nature of the adsorption.

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