



## Research paper

# High removal capacity of silver ions from aqueous solution onto Halloysite nanotubes

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## ABSTRACT

The adsorption of silver ions onto Halloysite nanotubes (HNTs) was investigated in aqueous solution in a batch system. The natural HNTs used as adsorbent in this work were initially characterized by TEM. The amounts of the silver ions adsorbed onto HNTs were influenced by initial silver ion concentration, temperature, pH, contact time and adsorbent dose.

Adsorption increased with increasing initial silver ion concentration, initial pH, and temperature. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models were considered to evaluate the rate parameters. The adsorption followed pseudo-second-order kinetic model with correlation coefficients greater than 0.999. The experimental isotherm data were analyzed using the Langmuir, Freundlich and Temkin equations. The Langmuir isotherm model showed significant fit to the equilibrium adsorption data and the maximum adsorption capacity of 109.79 mg g<sup>-1</sup> (99.8% removal) of silver ions was achieved. The thermodynamic parameters of activation such as Gibbs free energy, enthalpy and entropy were also evaluated. The results indicate that HNTs could be employed as effective nano-adsorbent for the removal of heavy metal ions.

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## 1. Introduction

Silver is a very useful raw material in various industries due to its excellent malleability, ductility, electrical and thermal conductivity, photosensitivity and antimicrobial properties. Significant amounts of silver are lost in the effluents discharged from such industries and due to the toxicity of silver to living organisms; the removal of this metal from wastewaters is an important concern (Mahmoud et al., 2010). Although some conventional methods for instance chemical precipitation (Kim et al., 2002), ion exchange resin (Hubicki et al., 2008), oxidation (Chen et al., 2013) and separation membrane (Chamoulaud and Bélanger, 2005) can remove silver ions from their effluents, they are partially not economical and are not efficient for low concentrations. Therefore, new techniques such as adsorption should be sought. Adsorption phenomenon in solution systems plays a vital role in many areas of practical environmental technology, which are mainly in water and wastewater treatment due to several advantages such as high efficiency, simple operation and easy recovery/reuse of adsorbent (Liu et al., 2009).

In recent years, natural mineral materials, due to their large surface area, high cation exchange capacity and low costs, have been studied for potential applications as environmental remediation agents to remove heavy metals from wastewater. Also nanoscopic materials are of great interests to be developed as efficient adsorbents for metal ions, because of their high surface area to unit mass ratios. Among these

nanomaterials, Halloysite nanotubes (HNTs) are cheap, abundantly available, and durable, with high mechanical strength and biocompatible (Yuri et al., 2008). Also various sorbents have been used in studies to remove Ag ions and the heavy metals from water and wastewater by sorption. Several studies have been proposed in the literature about the use of new sorbents, in relation with silver ion sorption from water solutions. These materials have some comparative advantages in contrast to common sorbent materials. Literature data are summarized in Table 1.

As seen in Table 1, there are researches all over the world, on the understanding of the mechanisms of removing Ag ions through new sorbents. HNT sorbents have been employed in literature. However, no studies on Ag<sup>+</sup> removal with the HNT nano-adsorbent were found. So in this study, we have considered it of great interest to assess the ability of commercially available Halloysite nanotubes for the removal of silver ions from aqueous solution and optimization of conditions for its maximum adsorption. To increase the efficiency of metal removal, various parameters have been studied. Also, the thermodynamic and kinetic parameters of the Ag<sup>+</sup> adsorption have been investigated.

## 2. Experimental details

### 2.1. Materials

Halloysite (premium grade) was obtained from New Zealand China Clays Ltd (New Zealand). Halloysite was first sieved (125 μm mesh) to remove granules to obtain 42% fine powder (HNT). A TEM image was obtained with a JEOL JEM-2100 (Japan). The metal adsorption capacities

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**Table 1**  
Comparison of maximum adsorption of Ag<sup>+</sup> ions onto various adsorbents.

Absorbents	$q_t$ (mg/g)	Reference
Polyacrylonitrile nanofiber mats	105.7	Pimolpun and Pitt (2010)
Valonia tannin resin	97.08	Yurtsever and Şengil (2012)
Natural bentonite	80	Hefne et al. (2010)
Alfalfa biomass	27.37	Herrera et al. (2003)
Conducting electroactive polymers	35	Ansari and Fallah Delavar (2008)
Calcium alginate beads	52	Torres et al. (2005)
Functionalized polyacrylonitrile	85.99	Kiani et al. (2011a,b)
Halloysite nanotubes	109.79	This study

of HNTs were measured by atomic adsorption spectrophotometer (AA 55B, Varian SLM) at room temperature.

## 2.2. Adsorption experiments

The 100-mL samples containing known concentration of silver ions and HNTs were added to Erlenmeyer flasks. The flasks were stirred with a rate of 300 rpm in a water bath (Pars Azma, Iran). The pH of the silver ion solutions was adjusted in the range of 4–6 with 0.1 N HCl by using a WTW (pH720, Germany) pH-meter with a combined pH electrode. The pH-meter was standardized with buffers before measurement. At the end of the adsorption period, the solution was centrifuged (Hettich, EBA20, Germany) for 10 min at 4000 rpm.

The amounts of silver ion adsorbed on HNTs at any time,  $t$ , were calculated from the concentrations in solutions before and after adsorption. At any time, the amount of silver ion adsorbed ( $\text{mg g}^{-1}$ ) ( $q_t$ ) by HNTs was calculated from the mass balance equation as follows:

$$q_t = V(C_0 - C_t)/W \quad (1)$$

where  $q_t$  is the amount of silver ions adsorbed into HNTs at any time ( $\text{mg g}^{-1}$ ),  $C_0$  and  $C_t$  are the concentration of silver ion before adsorption and after contact time ( $\text{mg L}^{-1}$ ), respectively;  $V$  is the volume of silver ion solution (L), and  $W$  is the mass of HNT sample used (g) (Kiani et al., 2011a,b). In order to determine the best kinetic model which fits the adsorption experimental data, the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were examined. The linear forms of these models can be described by Eqs. (2)–(4):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

$$q_t = k_i t^{1/2} + C \quad (4)$$

where  $q_e$  is the amount of the adsorbed silver ion at equilibrium per unit mass of the adsorbent ( $\text{mg g}^{-1}$ ),  $k_1$  ( $\text{min}^{-1}$ ),  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) and  $k_i$  ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) are the rate constants of the adsorption in pseudo-first-order (Eq. (2)), pseudo-second-order (Eq. (3)) and intraparticle diffusion models (Eq. (4)), respectively (Doğan et al., 2004; Taty-Costodes et al., 2003; Vadivelan and Kumar, 2005).

## 3. Results and discussion

In Fig. 1 TEM image of the Halloysite nanotubes is shown. A mainly hollow tubular structure is clearly visible from TEM images. The Halloysite is predominately tubular with a length of 0.5–1  $\mu\text{m}$  and an inner diameter of 10–20 nm.

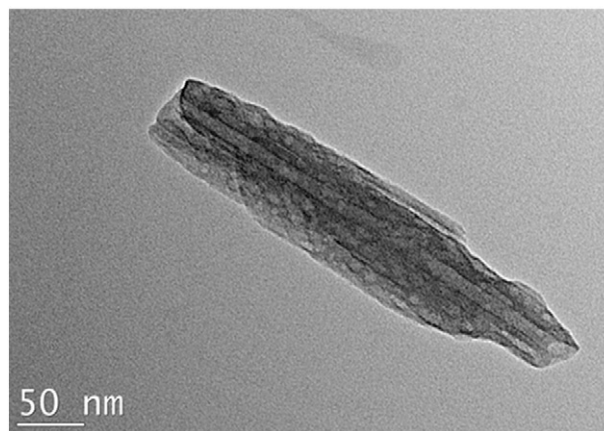
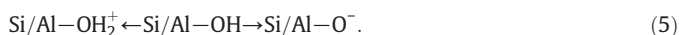


Fig. 1. TEM image of HNTs.

## 3.1. Adsorption

### 3.1.1. Effect of pH

pH of the solution plays an important role in the adsorption of metal ions from solution (Saha et al., 2010). As shown in Fig. 2, a consistent increase in adsorption capacity of the HNTs was noticed as the pH increased from 4 to 6. As shown in Fig. 2 the amount adsorbed does not change with an increase of the pH from 4 to 5, but increases at pH = 6. This is attributed to the electrostatic attraction of the positively charged silver ions with the negatively charged surface of HNTs. The surface of HNTs bears abundant Si–OH and Al–OH groups, which can ionize by Eq. (5):



With the decreasing pH, the negatively charged HNT sites tend to be saturated by protons, thereby the adsorption capacity decreases. In addition, the observed lower uptake in an acidic medium may be attributed to the partial protonation of the active groups and the competition of H<sup>+</sup> with silver ions for adsorption sites on HNTs (Luo et al., 2010).

### 3.1.2. Effect of contact time and initial silver ion concentration

The effect of initial silver ion concentration and contact time on the adsorption rate of silver ions onto HNTs is shown in Fig. 3. The amount of silver ions adsorbed at any time increases from 0.449 to 1.01  $\text{m mol g}^{-1}$  (48.11 (96.22 removal %) to 109.79 (99.8 removal %)  $\text{mg g}^{-1}$ ) by increasing the initial silver ion concentration from 50 to 110  $\text{mg L}^{-1}$ . Therefore, adsorption increases with increasing initial silver ion concentration. The

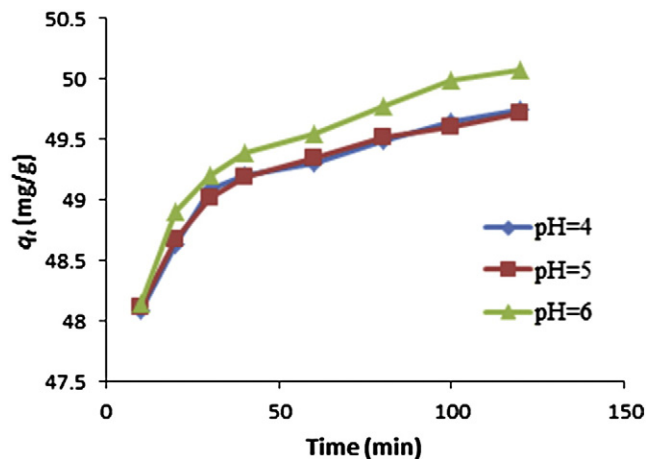


Fig. 2. Effect of contact time and initial pH on adsorption of silver ions onto HNTs from aqueous solutions.

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