

REMOVING OF As (V) FROM AQUEOUS SOLUTION USING NATURAL AND PRETREATED GLAUCONITE AND HALLOYSITE

Ismael Sayed ISMAEL & Sherif KHARBISH

Suez University, Faculty of Science, Geological Department, e.mail: Ismaelsayed@hotmail.com Tel: 02-182006962

Abstract: Adsorption of arsenic on clay surfaces is important for the natural and simulated removal of arsenic species from aqueous environments. In this investigation, two samples of clay minerals (glauconite and halloysite) in both untreated and acid activated treated forms were used for the sorption of arsenate from aqueous solution. Glauconite is mainly composed of illite/ smectite mixed layer, kaolinite and quartz. Halloysite is composed of halloysite, kaolinite, quartz, marcasite and trace amount of pyrite. Iron is existed as separated minerals (marcasite and pyrite) in the case of halloysite or present in the structure of glauconite, which play an important role in the adsorption of arsenic. Acid activation followed by calcination enhanced the adsorption capacity compared to the untreated clay minerals due to the increased surface area and pore volume. However, the increasing of acid activation leads to dissolution of iron from sorbent clay materials which in turn lead to decrease the adsorption capacity of As (V). The effects of initial As (V) concentration, contact time and pH on the adsorption of arsenic (V) by the untreated and treated glauconite and halloysite were investigated. Maximum adsorption capacity (about 93%) was recorded for treated halloysite at equilibrium conditions pH5, 240 minute contact time, arsenate concentration 0.90 mg/L, and at temperature 25°C. The adsorption kinetics of glauconite follow the Langmuir pseudo first-order model, while the adsorption kinetic of halloysite was neither fit with pseudo first-order kinetics model nor with pseudo second-order kinetics model, suggesting adsorption kinetics of halloysite should be further analysis.

Key Words: glauconite – halloysite – As(V) adsorption – acid activation , iron

1. INTRODUCTION

Arsenic is a minor terrestrial element in the earth's crust and is highest in marine shale materials, magmatic sulfides, and iron ores, where arsenic occurs as arsenopyrite (FeAsS), realgar (AsS), and orpiment (As₂S₃) (Tanaka, 1988; Huang, 1988). Arsenic has been known as a toxic element for centuries due to the risk to plants, animals and human health. It is known that arsenic is responsible for the development of liver, bladder, skin, and kidney cancer, and long-term intake of small doses of inorganic arsenic compounds causes in many other diseases (Chatterjee et al., 1995). The mean values of arsenic content in soils, the earth's crust, and sediments are 6, 1.5, and 7.7 mg kg⁻¹ respectively (Sparks, 1995). Natural waters contain low levels of total arsenic (about 1 to 10 µg/L) as Arsenate and/or As(III) (Williams, 2001). The natural oxidation of air-exposed sulfide minerals is one of the origins of crust chemical elements mobilization associated with the generation of acid mine drainage. Mobilization of arsenic in the environment arises also

from anthropogenic activities related to mining and ore processing, metallurgy, agriculture, wood preservation, and industry.

The World Health Organization (WHO), the European Union, the United States, and many other countries' governments have established 0.050 mg/L arsenic as the maximum contaminant level for total arsenic in potable water. However, there is evidence of adverse health effects at lower exposure levels. WHO thus promoted 0.010 mg/L arsenic as the new guideline value for arsenic in potable water (Williams, 2001).

Arsenic-contaminated waters are used by populations of some parts of the world, with large-scale disasters occurring in particular regions of Asia, Africa, and Central and South America (Williams, 2001; Chen et al., 1994) involving some millions of inhabitants. In some Bengal districts of India, arsenic ground water concentrations range between 0.05 and 1.25 mg/L, reaching 3.7 mg/L in some places (Chatterjee et al., 1995).

The two most important factors controlling the speciation of arsenic (and, to some extent, solubility)

are pH and redox potential. Under oxidizing conditions at pH less than 6.9, (H_2AsO_4) is the dominant species, whereas $(\text{HAsO}_4)^{2-}$ predominates at higher pH. Under reducing conditions at a pH value less than 9.2, the uncharged arsenite species (H_3AsO_3) is dominant. In contrast to the pH dependency of Arsenate, As (III) was found virtually independent of pH in the absence of other specifically adsorbed anions (Smedley & Kinniburgh 2002). Most often, As(III) is usually the predominant species under reducing conditions, whereas arsenate usually predominates under oxidizing conditions (Elizalde-Gonzalez et al., 2001). Most adsorption and chemical precipitation treatments require an oxidation pretreatment to convert As (III) into arsenate because arsenate usually adsorbs and reacts more strongly than As(III) (Ahmed, 2001).

Arsenic removal takes place by several methods such as ion exchange, membrane process, adsorption, or chemical precipitation. Among these methods adsorption of inorganic (As) compounds from aqueous system using both natural and synthetic sorbents, such as iron containing compounds (Ramaswami et al., 2001; Su & Puls, 2001), iron- or iron-manganese-modified zeolite (Jiménez-Cedillo et al., 2011), lanthanum compounds (Tokunaga et al., 1997), manganese oxides (Manning et al., 2002), Aqua-bindTM (Senapati & Alam, 2001), and granular ferric hydroxide (Pal, 2001). The adsorption of As species on clay surfaces could be important for economical aspects because most of natural clays and aluminosilicates fall into the low-cost and available materials (Lin & Puls, 2003; Doušová et al., 2005; 2006).

Clays are hydrous aluminosilicates that make up the colloid fraction ($<2 \mu$) of soil, sediment, rocks and water (Pinnavaia, 1983). The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), Brønsted and Lewis acidity, etc., have made the clays excellent materials for adsorption (Tanabe, 1981). Researchers have reported that acid activation followed by thermal treatment increases the adsorption capacity the clay minerals to a good extent (Alvarez & Garcia, 2003; Yavuz et al., 2003; Bhattacharyya, 2007). Such observations have stimulated a good number of studies in metal ion removal by using clay minerals and their modified forms as adsorbents.

In this study, two types of layered clay minerals 1:1 layer clay minerals “halloysite” and 2:1 layer clay minerals “glaucinite” were used as arsenic sorbents. Halloysite is a clay mineral similar in structure to kaolinite, having a 1:1 structure in which a silica tetrahedral sheet is joined to an alumina octahedral

sheet. Glaucinite has a structure with one dioctahedral sheet sandwiched between two silicon tetrahedral sheets (Nesse, 1991). The tetrahedral sheets are bonded together with potassium and sodium in a 12-fold coordination with oxygen from the tetrahedral sheets (Nesse, 1991). The dioctahedral layer in glauconite usually contains more Fe^{3+} along with significant amounts of Fe^{2+} and Mg^{2+} . The overall charge deficiency in glauconite caused by the divalent cations replacing trivalent cations in the octahedral layer is balanced by more silicon, Si^{4+} replacing iron, Fe^{3+} , in the tetrahedral layer. The structure also usually contains layers of expandable-type clay in variable proportions and may contain excess absorbed water (Nesse, 1991).

2. MATERIALS AND METHODS

Two samples of clay minerals were selected for this study, green clay “glaucinite” obtained from El Gidida area Egypt, and halloysite obtained from BlackJack, Utah U.S.A. Green clay and halloysite samples were treated by acid activation and calcination. Both untreated and treated samples were investigated in terms of their selectivity for As (V) removal from aqueous solution.

Acid activation of glauconite and halloysite was carried out by treating with 2 M HCl (E. Merck, Mumbai, India) by standard procedure (Espantaleon et al., 2003). 20 g of the clays (glaucinite and halloysite) were refluxed with 200 ml of 2 M HCl at about 100°C for 1, 2 and 4 hours respectively. The resulting clays (acid activated glauconite and halloysite) were centrifuged and washed with water several times till it was free of acid and dried at 90 °C in an air oven until constant weight was attained. All the clays were calcined before using them as adsorbents at 550°C for 5h.

Characterization of treated and untreated samples was carried out using x-ray diffraction (XRD), Infra Red (IR), x-ray fluorescent (XRF), surface area, and scanning electron microscope (SEM). X-ray diffraction was carried out using Philips diffractometer (PW1710) for powder sample and the clay fraction ($<2\mu\text{m}$), with scan speed 2°/min. X-ray fluorescence (XRF) analysis was done using a Philips type PW 1410 instrument. Infrared spectra were obtained using (FTIR) spectrometer (BIORAD) FTS 6000. The KBr pressed pellet technique was used, with a spectral range of 4000-400 cm^{-1} . Scanning electron micrographs were carried out using (Topcon) sm-300 scanning electron microscope. Surface area was determined using ASAP 2010 micrometrics.

The stock solution of arsenate As (V) 1000 mg/L was prepared from $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ salt, which

was subsequently used to prepare experimental solutions of specified concentrations. The concentration of arsenic in the aqueous solutions was determined by using a Perkin-Elmer (Model 2280) atomic absorption spectrophotometer (AAS) at 193.7 nm resonance line, using air–C₂H₂ flame.

The adsorption experiments were carried out in 100 ml Erlenmeyer flask by mixing clay sample and 50mL aqueous solution of As (V) ions and agitating the mixture in constant temperature water bath thermostat for a desired time interval. Solid suspension density was 40 g L⁻¹ for the samples. The mixture was centrifuged and supernatant was analyzed with atomic absorption spectrophotometer for unadsorbed arsenic remained in the solution. The pH of the adsorbate solution was adjusted, if necessary by adding 0.01N NaOH or 0.01 N HCl in drops.

Adsorption studies show that oxidation of arsenite to arsenate is necessary to achieve effective arsenic removal, (Gupta & Chen (1978). The oxidation of any As (III) to As (V) was carried out by adding drops of hydrogen peroxide.

2.1. Adsorption kinetic model

Attempt was carried out to describe adsorption kinetics of arsenic (V) by glauconite and halloysite. Langmuir model was used which can be written in a nonlinear form as:

$$C_e/q_e = 1/(q_m K_1) + (1/q_m) C_e$$

Where q_m = The monolayer adsorption capacity of the adsorbent (mg g⁻¹) (maximum amount adsorbed).

K_1 = The Langmuir adsorption constant (L mg⁻¹), that relates to the energy of adsorption.

C_e = The equilibrium metal ion concentration in the solution (mg L⁻¹).

q_e = The equilibrium metal ion concentration on the adsorbent (mg g⁻¹).

To describe the kinetics of the adsorption of arsenic by the glauconite and halloysite, two models were used pseudo-first-order-kinetic and pseudo-second-order-kinetic models. The pseudo first-order model is given by following equation:

$$\log (q_e - q_t) = \log q_e - K_1/2303 t$$

Where:

q_e (mg g⁻¹) = The amounts of arsenate (V) adsorbed on the glauconite or halloysite at equilibrium in mg g⁻¹.

q_t (mg g⁻¹) = The amounts of arsenate (V) adsorbed on the glauconite or halloysite at time in mg g⁻¹.

K_1 = Constant of pseudo first-order adsorption.

The pseudo second-order model is given as:

$$t/q_t = 1/K_2 q_e + 1/q_e$$

The value of q_e and K_2 can be determined from a slope and intercept respectively. Pseudo second order model has been successfully applied to several adsorption as

reported by McKay & Ho (1999); Otero et al., (2003).

3. RESULTS

3.1. Samples characterizations

The X-ray diffraction pattern of green clay (glauconite) and halloysite bulk samples are shown in (Figs. 1 and 2). The green clay is mainly composed of glauconite, kaolinite and quartz, while the halloysite is composed of halloysite, kaolinite, quartz, marcasite and trace amount of pyrite.

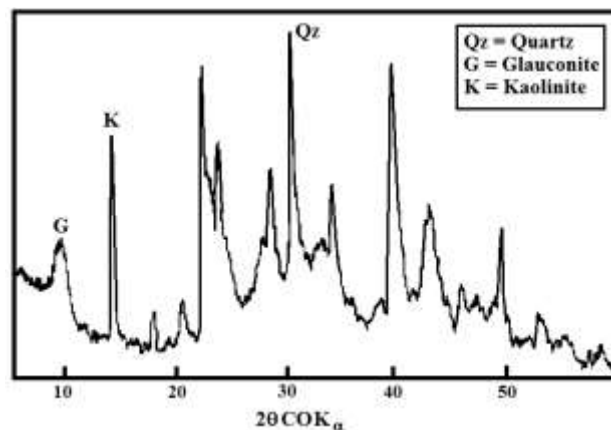


Figure 1. X-ray diffraction patterns of non-oriented glauconite sample

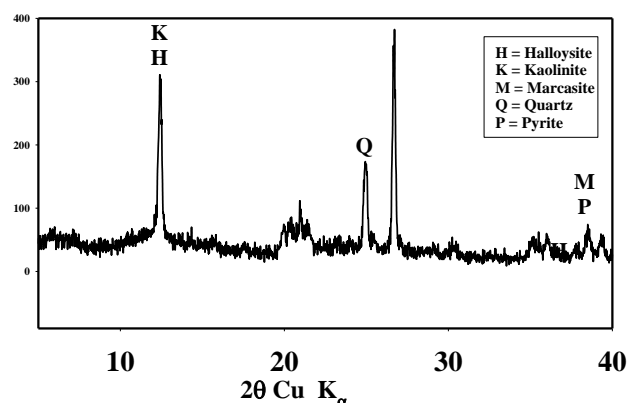


Figure 2. X-ray diffraction patterns of non-oriented halloysite sample.

A diagnostic feature of the X-ray pattern of halloysite is that the 11.02 reflection line at ~4.42 Å is more intense which revealed its tubular morphology (Wilson, 1999). The X-ray diffraction pattern of <2μm fraction of green clay (glauconite) and halloysite samples are shown in (Figs. 3&4). It is clear to note that, the green clay sample composed of illite/smectite mixed layer, after ethylene glycol solvation, basal reflections are broadened, especially at (001) plane from 9.7 to 15.95 Å. The swelling layered clay minerals were about 20% (Thompson & Hower, 1975). Upon heating to 550°C, basal

reflections are collapsed, and the reflection (001) sharpened at 9.8 Å peak. Meanwhile, the diffraction pattern of the (<2µm) fraction of halloysite shows a sharp (001) reflection, at about 7.14Å.

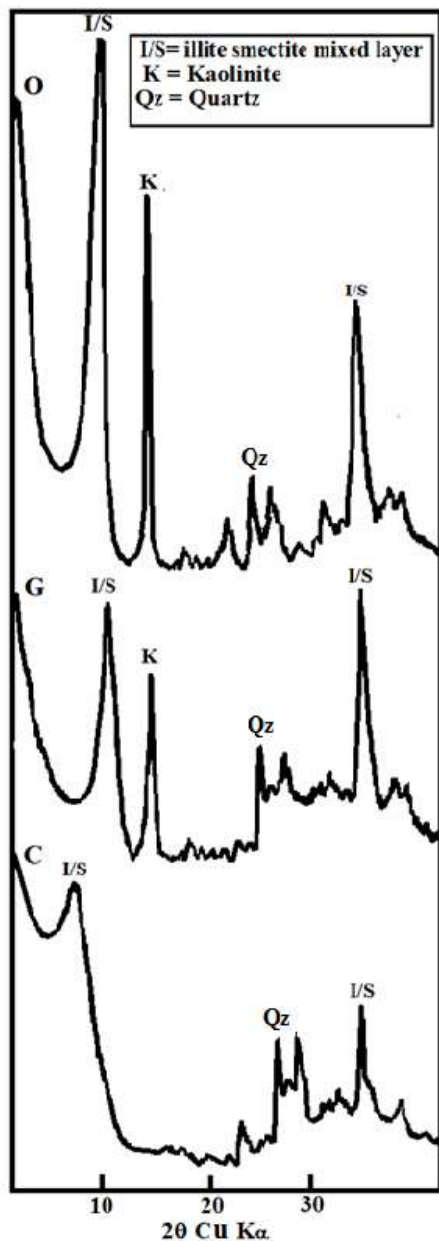


Figure 3. - X-ray diffraction patterns of <2µm glauconite sample. O = oriented, G = Glycolated, C = heated

Figure 4 illustrates the changes that occur in the halloysite XRD pattern on immediate treatment (within 60 min) with ethylene glycol and dimethyl formamide. The (001) reflection of halloysite expands to 10.8 Å and 10.2 Å corresponding to ethylene glycol and dimethyl formamide treatment, respectively. After these treatments, kaolinite appeared with its characteristic basal spacing (7.14Å). Upon heating up to 550°C the basal reflection of halloysite and kaolinite was disappeared.

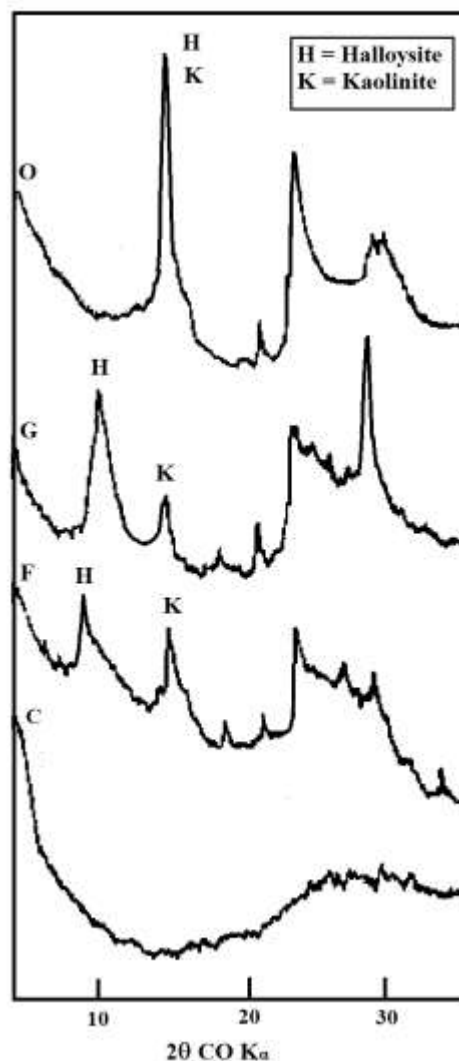


Figure 4. - X-ray diffraction patterns of <2µm halloysite sample. O = oriented, G = Glycolated, F = after dimethyl formamide treatment, C = heated

Figure 5 shows IR spectra of untreated and treated glauconite samples. Before acid activation two moderate intensity and broader OH-stretching bands at 3690 and 3627 cm^{-1} , two small inflexions occur between them as well as the deformation band at 803 cm^{-1} . The Si-O stretching region comprises two absorption bands at 1100 and 1034 cm^{-1} , and low intense band at 693 cm^{-1} , Si-O-Fe deformation bands at 530 cm^{-1} for Si-O and at 491 cm^{-1} for Si-O-Mg. The low intensity of the deformation band at 1630 cm^{-1} reveals the interlayer water content of the glauconite.

By acid activation, the most prominent change was broadening of all bands, diminishing OH stretching bands and shifting in the Si-O stretching region. The Si-O-Si band at 930 cm^{-1} was diminished and the intensity of the Si-O vibration band of amorphous Si-O near 1100 cm^{-1} increased during the course of acid dissolution. The band at 930 cm^{-1} was

absent from the spectrum after 4 h. Further, the increased intensity of the band at 792 cm^{-1} and 470 cm^{-1} attributed to the Si–O vibration of amorphous silica, indicating an increased amount of amorphous silica as acid dissolution progresses (Moenke, 1974).

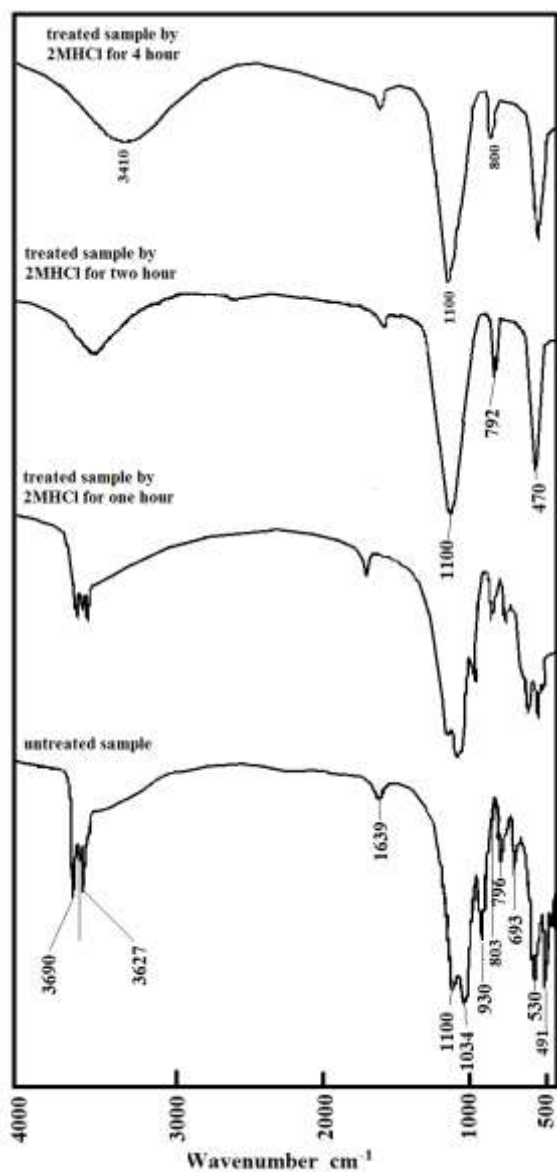


Figure 5. IR spectra of untreated and treated glauconite sample.

Figure 6 shows IR spectra of untreated and treated halloysite samples. Before acid activation spectrum of halloysite is characterized by two moderate intensity and broader OH-stretching bands at 3676 and 3649 cm^{-1} ; two small inflexions occur between them. The absorption band at 3551 cm^{-1} was assigned to OH stretching. The Si–O stretching region comprises two absorption bands at 1207 and 1030 cm^{-1} . The Al–OH bond at 939 cm^{-1} was assigned to the inner OH- surface. The stretching band Si–O at 794 cm^{-1} was broad and low intensity.

The broad band at 499 cm^{-1} was assigned to the Si–O–Si bending. The low intensity of the H–O–H deformation band at 1635 cm^{-1} reveals the interlayer water content of the halloysite.

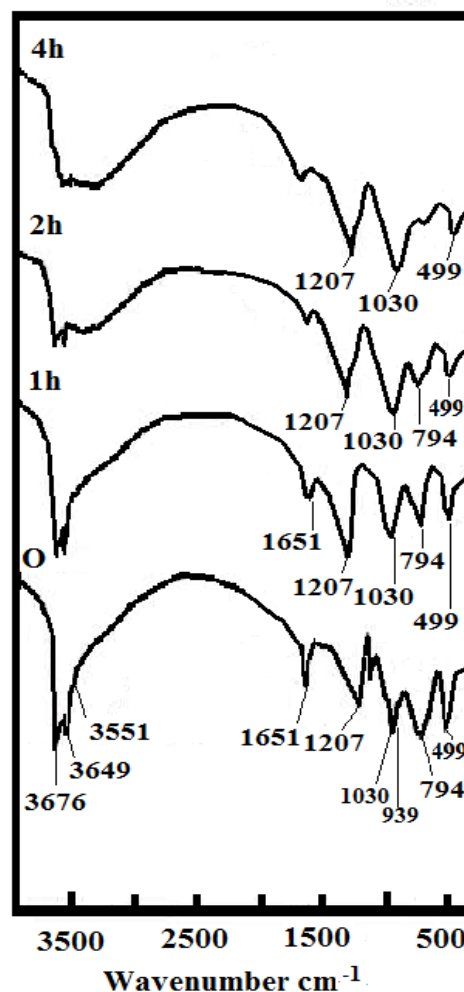


Figure 6. IR spectra of untreated and treated halloysite sample. O = Untreated sample, treated sample by 2M HCl for one hour = 1h, two hour = 2h, four hour = 4h

After acid treated with 2M HCl, the intensity of the absorption bands as well as the area of the vibrations decreased during prolonged acid attack. The intensity of the OH bands at 939 cm^{-1} decreased during prolonged acid attack displays the content of not reacted Al. The intensity of the bridging Si–O–Al vibrations at 794 cm^{-1} , as well as the intensity of the tetrahedral Si–O–Al vibration at 499 cm^{-1} decreased during prolonged acid attack. Only a small and broad band at 499 cm^{-1} still existed after 4 h. This reveals that, the treatment of halloysite with acid causes preferential release of octahedral Al ions from the halloysite structure with formation of additional Al–OH and Si–OH bonds without disturbing the mineral structure (Vicente et al., 1996).

Table 1- The chemical compositions of treated and untreated glauconite and halloysite

Elements oxides	Untreated glauconite	Treated glauconite with 2HCl			Untreated halloysite	Treated halloysite with 2HCl		
		1h	2h	4h		1h	2h	4h
SiO ₂	57.56	60.54	62.14	64.75	39.97	40.62	41.63	43.89
Al ₂ O ₃	7.34	8.24	12.86	15.93	36.75	37.92	39.51	40.75
Fe ₂ O ₃	19.73	13.21	7.59	3.17	11.56	7.64	3.83	1.97
MgO	2.25	1.05	0.67	0.35	0.12	0.09	0.07	0.07

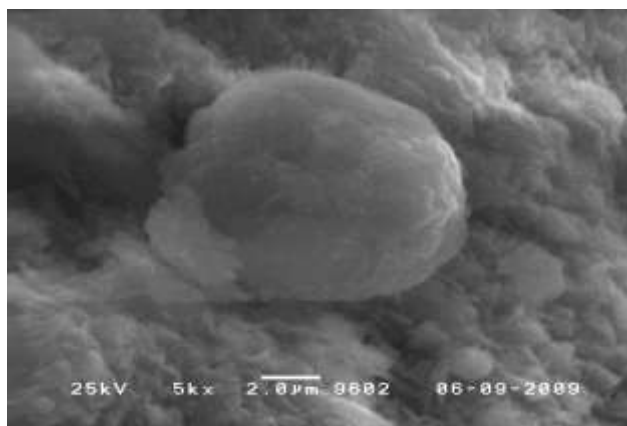


Figure 7a. SEM micrograph shows the glauconitic material as highly fractured pellets.

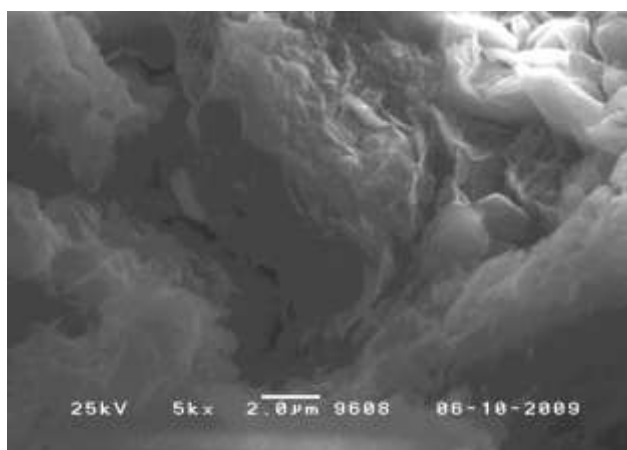


Figure 7b. SEM micrograph shows the glauconitic materials consist of spherical aggregates of parallel platelets appears as highly crumpled and curled flakes.

The chemical compositions of treated and untreated glauconite and halloysite are listed in table (1). It is clear to note that the iron oxide percentage is decrease in both glauconite and halloysite by progressing of acid activation. In the glauconite iron is constituent of its structure, while in halloysite sample iron presents as separated minerals marcasite and pyrite. On the other hand, as the acid activation period increased, the ratio of Si/Al increased due to dealumination and Si/Al ratio increased. The BET surface area of untreated glauconite was 43.7 m²/g. After treated with 2MHCl for 1h, 2h and 4h, the surface area increases to 47.1, 52.4 and 64.4 m²/g

respectively. On the other hand, the surface area of untreated halloysite is 18.2 m²/g. After acid activation for 1h, 2h and 4h it increases to 23.6, 26.1 and 29.3 m²/g respectively. Activation of glauconite and halloysite by acid treatment and subsequent calcination has been shown effective in limiting possible decomposition of the crystalline structure and increasing the specific surface area (Sabah et al., 2002). The acid treatment opens up the edges of the platelets and as a consequence, the surface area and the pore diameter increase (Volzone et al., 1999).

SEM micrographs show the glauconitic material as highly fractured pellets with altered rims (Fig. 7a). The pellets consist of spherical aggregates of parallel platelets appears as highly crumpled and curled flakes (Fig. 7b). Halloysite identified by a typical tubular shape (Romero et al., 1992) appears as well developed tubes reaching 4 µm in length and 0.03 µm in diameter (Fig. 7c).

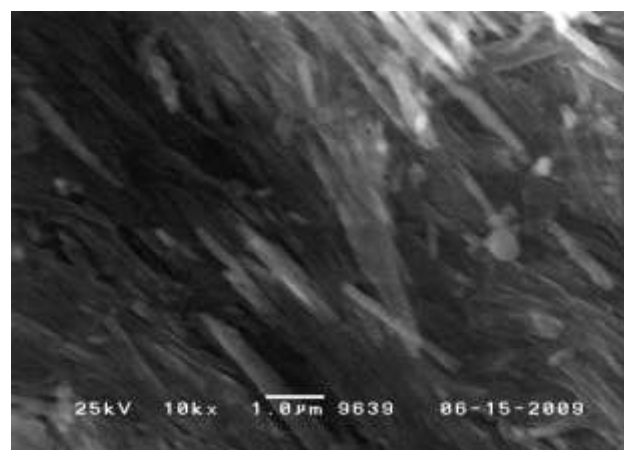


Figure 7c. SEM micrograph shows tubular shape of halloysite.

3.2. Evaluation of the adsorption capacity

3.2.1. Effect of contact time

Variation of removal of arsenate with contact time for studied samples (untreated and treated glauconite and halloysite with 2M HCl, respectively) was measured by mixing 2g of sample with arsenate 0.90 mg/L, at 25°C, pH 5 for interaction time 20, 40, 60, 80, 160, 180, 240, 300, 360 minute respectively (Fig. 8).

Notably the adsorption was rapid in the initial stages and the rate decreases and leveled off with time till the equilibrium is attained in 180 minutes (Fig. 8). There was no increase in arsenate uptake after 240 minute and this is taken as the equilibrium time.

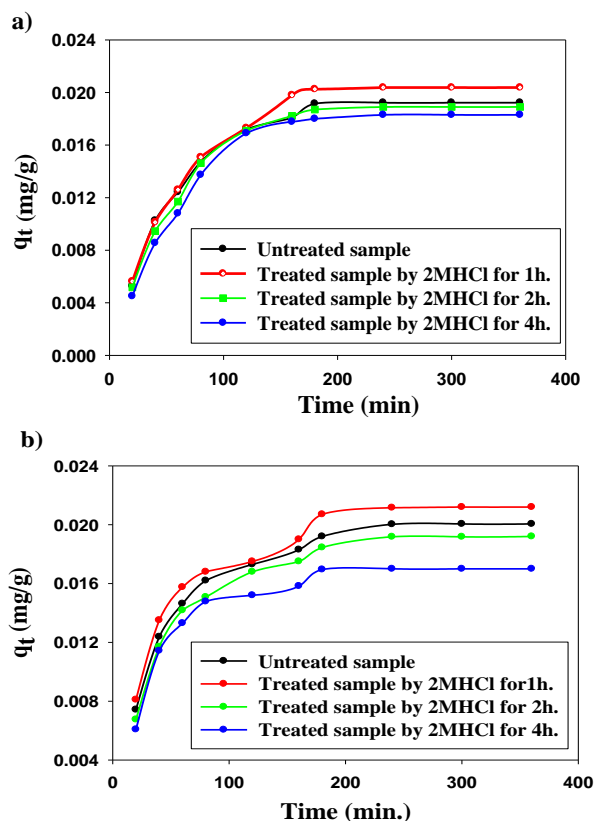


Figure 8. Effect and contact time on adsorption of arsenic (V) by untreated and treated a) glauconite b) halloysite

3.2.2. Effect of initial concentration

The influence of initial As (V) concentration by untreated and treated glauconite and halloysite samples was studied at room temperature 25°C, for fixed pH value of 5, at interaction time 240 minute and sorbent amount 2g with varying As(V) concentration from 1.5 to 0.50 mg/L (Fig. 9). It was observed that the uptake capacity of pretreated halloysite and glauconite with 2M HCl for one hour was higher than raw one.

The amount of As(V) adsorbed increased with an increase in the initial adsorbate concentration from 0.50 to 0.90 mg/L. However, the efficiency of As(V) removal is affected by the initial concentration, with decreasing removal percentages as the concentration increases from 0.90 to 1.5 mg/L. This results show that the efficiency in removal of arsenic is higher with low initial concentration (about 90% and 93% for treated glauconite and halloysite by 2MHCl for one hour) and gradual decrease at higher initial concentration of arsenic. This could be explained by at a low initial metal ion concentration, the ratio of the number of As

(V) ions to the number of available adsorption sites is small and consequently the adsorption is independent of the initial concentration, but as As (V)/sorbent ratio increases, the exchangeable sites are saturated, resulting in a decrease in the adsorption efficiency (Mishra & Patel, 2009).

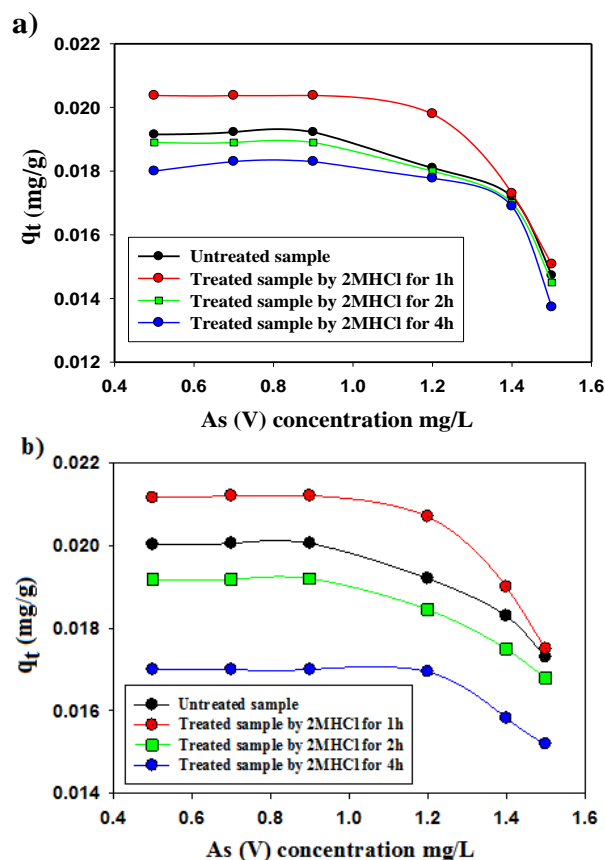


Figure 9. Effect of initial concentration on adsorption of arsenic (V) by untreated and treated a) glauconite b) halloysite.

3.2.3. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process (El-Hendawy, 2009; Abdel-Halim et al., 2003). In clay aqueous systems the potential of surface reactivity is determined by the activity of ions (H^+ or OH^-) which react with the mineral surface. As such pH plays an important role in controlling the adsorption of arsenic at the clay-solution interface. Such interface on acid-base dissociation develops positive or negative charges on the surface depending on the pH of the system (Worrl, 1968; Meenakshi & Viswanathan, 2007). In order to investigate the effects of pH on metal ion adsorption, 2g of clays (untreated and treated glauconite and halloysite) was mixed with arsenate 0.90 mg/L, at temperature 25°C, at interaction time 240 minute at various pH values ranging from 2 to 9. The plot of removal of arsenate at various pH ranges as shown in figure 10. It clearly indicates that the

removal of arsenic for treated and untreated clays (glaucanite and halloysite) samples was influenced by the pH of the system. There was no removal of As (V) at pH lower than 3 and a gradual increase in adsorption with increase in pH from 3 to 5 with maximum adsorption at pH 5. The adsorption of As(V) decreased with increasing solution pH from pH 6 to 9. The slight increase adsorption of arsenate above pH 9 may be related to dissolution of the clay minerals at elevated pH values.

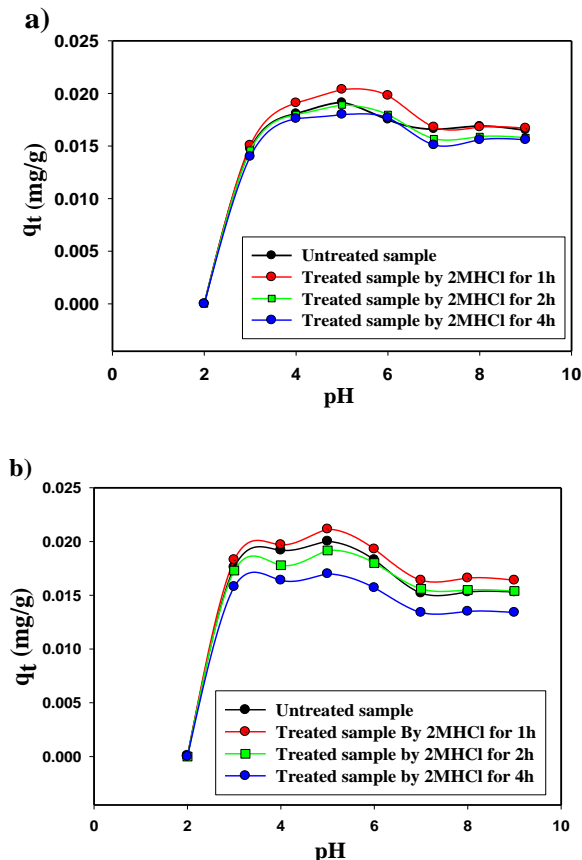


Figure 10. Effect of pH values on adsorption of arsenic (V) by untreated and treated a) glaucanite b) halloysite.

3.2.4. Determination of the adsorption capacity

The maximum adsorption capacity (q_e) of arsenate (V) by the untreated glaucanite and halloysite was 0.0192 mg g^{-1} and 0.02 mg g^{-1} , respectively. Treated glaucanite and halloysite for one hour reported maximum adsorption capacity about 0.0204 mg g^{-1} and 0.0212 mg g^{-1} , respectively.

3.2.5. Adsorption kinetic

Adsorption rate of glaucanite and halloysite depends on the physical or chemical characteristic of the adsorbent and also on the operating conditions (Dang et al., 2009). Figure (11), show pseudo-first-order kinetic adsorption arsenic (V) by untreated and treated glaucanite and halloysite. The

values of K_1 and q_e were calculated from the slopes and intercepts of the plots, respectively. The data obtained are presented in table 2.

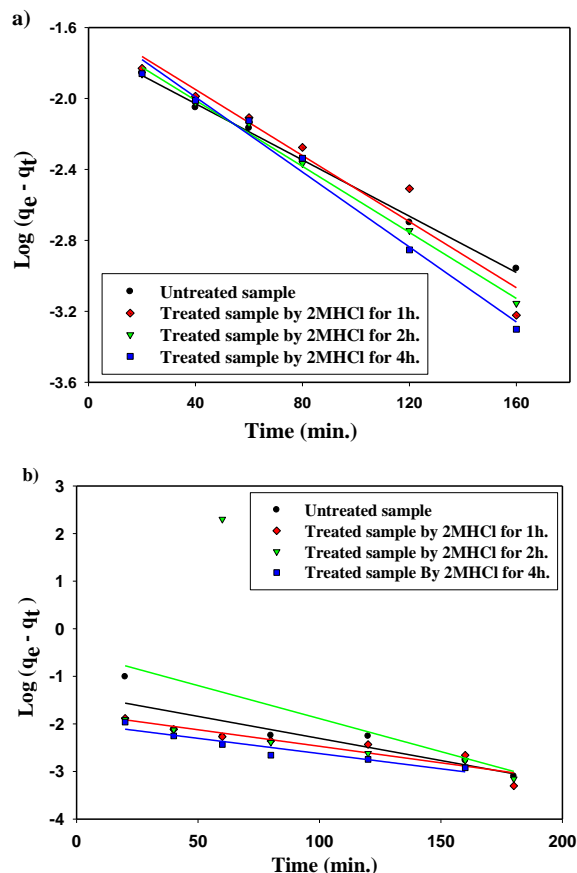


Figure 11. Pseudo-first-order kinetic adsorption of As (V) by untreated and treated a) glaucanite b) halloysite

As it can be seen from table (2), the experimental data were well correlated to the Langmuir model. This suggested that Langmuir model could very well explain the adsorption process of As (V) ion on untreated and treated glaucanite. Treated glaucanite for one hour exhibited greater maximum adsorption capacity (q_e) and stability constant (K_1) for the adsorption process of As (V) ion. The linearity with high R^2 values indicates that the system follows pseudo first-order kinetics.

On the other hand, it can be seen from linear regression correlation coefficient of untreated and treated halloysite, R^2 values for the first order kinetic was not large enough to fit with the experimental data. Therefore, adsorption kinetics of the process should be further analysis. However, the R^2 value of treated halloysite samples for four hours showed relatively high R^2 , suggesting system belong to first pseudo order kinetics. Figure 12 show pseudo-second-order kinetic adsorption arsenic (V) by untreated and treated glaucanite and halloysite.

Table 2- Langmuir pseudo-first-order parameters

Absorbents type	q_e mg/g experimental	q_e mg/g theoretical	K_1 L/g	R^2
Untreated glauconite	0.0192	0.194	$- 8.9 \times 10^{-3}$	0.996
Treated glauconite for 1h	0.0204	0.0254	$- 9.3 \times 10^{-3}$	0.946
Treated glauconite for 2h	0.0189	0.023	$- 9.3 \times 10^{-3}$	0.995
Treated glauconite for 4h	0.0183	0.0254	$- 1.04 \times 10^{-2}$	0.986
Untreated halloysite	0.020	0.042	$- 9.3 \times 10^{-3}$	0.750
Treated halloysite for 1h	0.0212	0.017	$- 7.0 \times 10^{-3}$	0.863
Treated halloysite for 2h	0.0192	0.31	$- 1.4 \times 10^{-2}$	0.206
Treated halloysite for 4h	0.0170	0.011	$- 6.4 \times 10^{-3}$	0.901

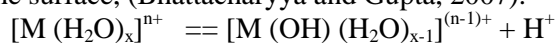
The values of K_2 and q_e were calculated from the slopes and intercepts of the plots, respectively. The data obtained are presented in table 3.

As shown in the table 3, the low values of R^2 and rate constant for untreated and treated glauconite and halloysite suggested that pseudo second order kinetic model was not suitable to describe the adsorption kinetic of As (V) by glauconite and halloysite.

4. DISCUSSIONS

Most of the clay minerals e.g. glauconite and halloysite contains cations and anion on their surface, held through the process of adsorption. These ions can be exchanged with other ions e.g. arsenic without affecting the clay mineral structure. Acid activation followed by calcination of the clays has made the clays excellent adsorbent materials.

Such treatments can often replace exchangeable cations with H^+ ions and release Al^{3+} and other cations out of both tetrahedral and octahedral sites, but leaving the SiO_4 groups largely intact (Theocharis et al., 1988; Rodrigues, 2003). The Bronsted acidity formed by dissociation of water molecules of hydrated exchangeable metal cations on the surface, which arises from H^+ ions on the surface, (Bhattacharyya and Gupta, 2007):



The Bronsted acidity may also arise if there is a net negative charge on the surface due to the substitution of Si^{4+} by Al^{3+} in some of the tetrahedral positions and the resultant charge is balanced by H_3O^+ cations. The Lewis acidity arises from exposed trivalent cations, mostly Al^{3+} at the edges, or Al^{3+} arising from rupture of Si-O-Al bonds, or through dehydroxylation of some Bronsted acid sites.

The edges and the faces of clay particles can absorb anions, cations, non-ionic and polar contaminants from natural water. The mechanism of arsenic adsorption using clay minerals could be attributed mainly by both adsorption and chemical

reaction. Affinity adsorption includes molecular-surface interaction and electrostatic interaction (i.e. ion exchange, coulombic attraction). The chemical reaction includes ligand exchange, surface complexation, covalent bonding and Van der Waals force (Gupta & Chen, 1978; Prasad, 1994; Edwards, 1994).

On the other hand, presence of ions like Fe^{3+} in octahedral positions, or adsorbed oxygen, the clay minerals behaves as oxidizing agent, while in presence of ions like Fe^{2+} in octahedral positions the clay mineral behaves as reducing agent (Van Olphen, 1977).

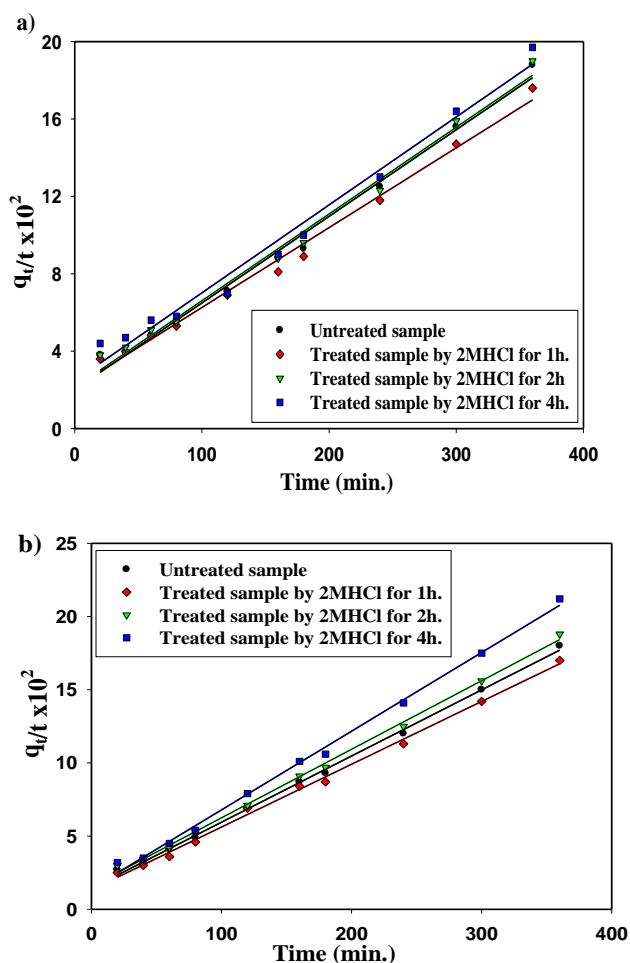


Figure 12. Pseudo-second-order kinetic adsorption of As (V) by untreated and treated a) glauconite b) halloysite

Table 3- Langmuir pseudo-second-order parameters

Absorbents type	q_e mg/g experimental	q_e mg/g theoretical	K_2 L/g	R^2
Untreated glauconite	0.0192	4.9×10^{-4}	44.74	0.991
Treated glauconite for 1h	0.0204	4.7×10^{-4}	41.43	0.991
Treated glauconite for 2h	0.0189	4.7×10^{-4}	45.04	0.990
Treated glauconite for 4h	0.0183	4.0×10^{-4}	45.42	0.985
Untreated halloysite	0.020	6.7×10^{-4}	45.16	0.998
Treated halloysite for 1h	0.0212	7.7×10^{-4}	42.95	0.996
Treated halloysite for 2h	0.0192	6.3×10^{-4}	46.77	0.998
Treated halloysite for 4h	0.0170	3.4×10^{-4}	34.42	0.434

In the present studied, iron that present in the structure of the clay minerals as in case of glauconite or separated minerals marcasite and pyrite associated with halloysite play an important role for remove of arsenic. Arsenate exists in solution as negative ions (Bard et al., 1985), the adsorption of As (V) may be the result of electrostatic attraction between anionic As (V) and positively charges iron on the surface of glauconite or marcasite. The negatively charged arsenic ions and positively charged adsorbent surface (glauconite and marcasite) favor the arsenic adsorption by electrostatic attraction (Ronald, et al., 2005; Prasenjit & Mohanty, 2007).

On the other hand, As (V) adsorbed onto hydrated Fe oxides/hydroxides from aqueous solution can yield the surface complexes (Goldberg, 2002). Doušová et al., (2006) reported that presence of Fe^{3+} species on the particle surface or in isolated particles has great affinity to adsorb As(V) to form more stable inner-sphere complexes or ferrihydrite. In spite of acid activation followed by calcination enhanced the adsorption capacity compared to the untreated clay samples due to the increased surface area and pore volume. The progression of acid activation lead to dissolution of iron from sorbent materials lead to decrease the adsorption capacity of As (V) reveals the main role of iron in removal of As (V). The relatively high adsorption capacity of halloysite compared with glauconite suggested the main role of separated iron minerals in the adsorption of As (V) rather than the clay minerals. Glauconite and halloysite samples are heterogeneous materials with a number of components to which the arsenic (V) species in solution may show different affinities, which the nature and strength of the bonds established between the arsenic (V) species and the different phases of the sorbent cannot be the same. Therefore, arsenic species may sorb preferentially onto some components of clay deposit to which they show greater affinity. This aspect would directly affect the adsorption of arsenic (V) and turn would affect the net efficiency of the removal process.

Adsorption of arsenic (V) was affected by initial concentration of As (V), pH and contact time. The

maximum arsenic adsorption capacity occurs at pH 5. This may be attributed to formation of ferric hydroxide. Ferric hydroxide has greater affinity to adsorb arsenic from its as well as its formation is more favorable at low pH (Ahmed, 2001).

Maximum As (V) adsorption capacity about 93% for treated halloysite for 1h, whereas it was about 90% for treated glauconite for 1h at pH 5 after mixing for 240 minute, under atmospheric conditions. The highest adsorption capacity of halloysite may be attributed to separated iron minerals, as well as formation of amorphous phases of aluminum hydroxide or ferric hydroxide has the highest adsorption capacity for arsenic, they have highest surface area (Saha et al., 2005; Wilkie & Hering 1996).

The kinetics of the As(V) adsorption on the glauconite was found to follow a pseudo-first-order rate equation. The disconformities between experimental data of halloysite and the model values of pseudo- first – order or pseudo-second order was expressed by the low correlation coefficient R^2 , K_1 and K_2 suggested adsorption kinetics of the process should be further analysis.

5. CONCLUSIONS

Both glauconite and halloysite and their acid activated forms are capable of removing As (V) ions from aqueous solution. In both samples iron is present. In the case of glauconite iron exists in its structure, whereas for halloysite iron exists as separated minerals marcasite and pyrite, which the iron plays an important role in As (V) adsorption. Acid activation followed by calcination enhanced the adsorption capacity compared to the untreated clay minerals due to the increased surface area and pore volume. However, the progression of acid activation lead to dissolution of iron from sorbent materials lead to decrease the adsorption capacity of As(V). The relatively high adsorption capacity of halloysite compared with glauconite suggesting the main role of separated iron minerals in the adsorption of As(V) rather than the clay minerals. Maximum adsorption capacity (about 93%)

was recorded for treated halloysite by 2M HCl for one hour at equilibrium conditions 5 pH, 240 minute contact time arsenate concentration 0.90 mg/L, and at temperature 25°C. Arsenic (V) – glauconite adsorption data closely follows the Langmuir model (pseudo first-order kinetics model) compared to the Arsenic (V) – halloysite adsorption data were not fitted with pseudo first-order kinetics model nor pseudo second-order kinetics model, suggesting adsorption kinetics of the process should be further analyzed.

ACKNOWLEDGMENTS

The authors are deeply grateful to Professor J.D. Miller, Department of Metallurgical Engineering, College of Mines and Earth Sciences, University of Utah, U.S.A. and Dr. I. Megahed, Chemical Department, Faculty of Science, Suez University, Egypt, for their helpful and facilitates.

REFERENCES

- Abdel-Halim, S.H., Shehata, A.M.A. & El-Shahat, M.F., 2003. *Removal of lead ions from industrial waste water by different types of natural materials*. Water Res 37(7), 1678–1683
- Ahmed, F.M., 2001. *An overview of arsenic removal technologies in Bangladesh and India*. In: M. Feroze Ahmed. (Eds). *Technologies for Arsenic Removal from Drinking Water*. A compilation of papers presented at the International Workshop on Technologies for Arsenic Removal from Drinking Water. Bangladesh University of Engineering and Technology, Dhaka, Bangladesh and the United Nations University, Tokyo. 251-269
- Alvarez-Ayuso, E. & Garcia-Sanchez, A. (2003) *Removal of heavy metals from waste waters by natural and Na-exchanged bentonites*. Clays Clay Miner., 51, 475–480.
- Bard, A.J., Parsons R. & Jordan, J. 1985. *Standard Potentials in Aqueous Solutions*. Marcel Dekker, New York, p. 162.
- Bhattacharyya, K.G., 2007. *Adsorption of Co(II) from Aqueous Medium on Natural and Acid Activated Kaolinite and Montmorillonite*, Separation Science and Technology, 42, 3391–3418.
- Bhattacharyya, K.G. & Gupta, S.S., 2007. *Removal of hazardous metals from water by clays*. Hazardous Materials and Waste water pp. 79-125.
- Chatterjee, D., Das, B.K., Mandal, T.R., Chowdhury, G., Samanta, D., Chakraborti, J., 1995. *Arsenic in Ground Water in Six Districts of West Bengal, India: The Biggest Arsenic Calamity in the World Part I. Arsenic Species in Drinking Water and Urine of the Affected People*. Analyst 120, 643–650.
- Chen, S.L., Dzen, S.R., Yang, M.H., Chlu, K.H., Sheih, G.M. & Wal, C.M., 1994. *Arsenic species in groundwaters of the Blackfoot Disease area, Taiwan*. Environ. Sci. Technol., 28, 877-881.
- Dang, S.V., Kawasaki, J., Abella, L., Auresenia, J., Habaki, H., Gaspillo, P.D. & Vu, Q., 2009. *An Investigation on the removal of Arsenic from Simulated Groundwater by Adsorption using Iron and Iron Oxide (III)*. Journal of Environmental Science for Sustainable Society, 3, 19-28.
- Doušová, B., Koloušek, D., Kovanda, F., Machovič, V. & Novotná, M., 2005. *Removal of Arsenate species from extremely contaminated mining water*, Appl. Clay Sci. 28(1–4), 31–43.
- Doušová, B., Grygar, T., Martaus, A., Fuitová, L., Koloušek, D. & Machovič, V., 2006. *Sorption of AsV on aluminosilicates treated with FeII nanoparticles*, Journal of Colloid and Interface Science 302, 424–431.
- Edwards, M., 1994. *Chemistry of arsenic removal during coagulation and Fe-Mn oxidation* J. American Water Works Association, 86(9), 64-87.
- El-Hendawy, A.A., 2009. *The role of surface chemistry and solution pH on the removal of Pb²⁺ and Cd²⁺ ions via effective adsorbents from low-cost biomass*. J Hazard Mater 167(1–3), 260–267.
- Elizalde-Gonzalez, M.P., Mattusch, J., Wennrich, R. & Morgenstern, P., 2001. *Sorption on natural solids for arsenic removal*. Chemical Engineering Journal. 81, 187-195.
- Espantaleon, A.G., Nieto, J.A, Fernandez, M. & Marsal, A., 2003. *Use of activated clays in the removal of dyes and surfactants from tannery wastewaters*. Applied Clay Science, 24, 105-110.
- Goldberg, S., 2002. *Competitive adsorption of arsenate and arsenite on oxides and clay minerals*. Soil Sci. Soc. Am. J. 66, 413-421.
- Gupta, S.K., & Chen, K.Y., 1978. *Arsenic removal by adsorption*. Journal of Water Pollution Control Federation, 50, 493-506.
- Huang, Y.C., 1988. *In Arsenic in the environment, part I: Cycling and characterization*; Nriagu, J.O., Ed.; Wiley-Interscience: New York., 16-26 .
- Jiménez-Cedillo, M.J., Olguín, M.T., Fall, Ch. & Colín A. 2011. *Adsorption capacity of iron- or iron-manganese-modified zeolite-rich tuffs for As(III) and As(V) water pollutants*. Applied Clay Science 54, 206–216.
- Lin, Z., Puls, R.W., 2003. *Potential indicators for the assessment of arsenic natural attenuation in the subsurface*, Adv. Environ. Res. 7, 825–834.
- Manning, A.B., Fendorf, E.S., Bostick, B. & Suarez, L.D., 2002. *Arsenic (III) Oxidation and Arsenic (V) Adsorption Reactions on Synthetic Birnessite*. Environmental Science and Technology. 36(5), 976-981.
- McKay, G. & Ho, Y.S., 1999. *The sorption of lead(II) on peat*, Journal of Water Resources, 33, 578-584.
- Mishra, P.C. & Patel, R.K., 2009. *Removal of lead and zinc ions from water by low cost adsorbents*. J Hazard Mater 168, 319–325.
- Meenakshi, S. & Viswanathan, N., 2007. *Identification of selective ion-exchange resin for fluoride sorption [J]*. Journal of Colloidal and Interface Science. 308, 438–450.
- Moenke, H.H.W., 1974. *Silica, the three-dimensional silicates, borosilicates and beryllium silicates*. In: Farmer, V.C. _Ed., *Infrared Spectra of Minerals*. The Mineralogical Society, London, pp. 365–382.
- Nesse, W.D., 1991. *Introduction to Optical Mineralogy*, Oxford Press 1991.pp1-370.

- Otero, M., Rozada, F., Calvo, L.F., Garcia, A.I. & Moran, A., 2003. Kinetic and Equilibrium modeling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges, *Journal of Biochemical Engineering* 15, 59-68.
- Pal, B.N., 2001. *Granular Ferric Hydroxide for Elimination of Arsenic from Drinking Water*. In: M. Feroze Ahmed et al. 2001 (Eds). *Technologies for Arsenic Removal from Drinking Water*. A compilation of papers presented at the International Workshop on Technologies for Arsenic Removal from Drinking Water. Bangladesh University of Engineering and Technology, Dhaka, Bangladesh and the United Nations University, Tokyo., 59-68.
- Pinnavaia, T.J., 1983. *Intercalated clay catalysts*. *Science*, 220, 365-371.
- Prasad, G., 1994. *Removal of As (V) from aqueous systems by adsorption onto geological materials*. *Arsenic in the Environment*, John Wiley & Sons, New York, U.S.A, 26, 33-154.
- Prasenjit, M.B.M. & Mohanty, C.B. 2007. A laboratory study for the treatment of arsenic, iron, and manganese bearing ground water using Fe^{3+} impregnated activated carbon: Effects of shaking time, pH and temperature. 1. *Hazard. Mater.*, 144, 420-426.
- Ramaswami, A., Tawachsupa, S. & Isleyen, M., 2001. Batch-mixed iron treatment of high arsenic waters. *Water Research*. 35(18), 4474-4479.
- Rodrigues, M.G.F., 2003. *Physical and catalytic characterization of smectites from Boa-Vista, Paraíba, Brazil*. *Cerâmica*, 49(2003), 146-150.
- Romero R., Robert M., Elsans F. & Garcia C. 1992. Abundance of halloysite neoformation in soils developed from crystalline rocks. *Contribution of transmission electron microscopy*. *Clay Minerals*, 27, 35-46.
- Ronald, L., Vaughan, J. & Brian, E. R., 2005. Modeling As(V) removal by a iron oxide impregnated activated carbon using the surface complexation approach. *Journal of Hazardous Materials*, B126, 198-201.
- Saha, B., Bains, R. & Greenwood, F., 2005. *Physicochemical Characterization of Granular Ferric Hydroxide (GFH) for Arsenic(V) Sorption from Water*. *Separation Science and Technology*, 40(14), 2909-2932.
- Senapati, K. & Alam, I., 2001. *Apyron Arsenic Treatment Unit. Reliable Technology for Arsenic Safe Water*. In: M. Feroze Ahmed et al. 2001 (Eds). *Technologies for Arsenic Removal from Drinking Water*. A compilation of papers presented at the International Workshop on Technologies for Arsenic Removal from Drinking Water. Bangladesh University of Engineering and Technology, Dhaka, Bangladesh and the United Nations University, Tokyo., 59-68.
- Smedley, P.L. & Kinniburgh, D.G., 2002. A review of the source, behavior and distribution of arsenic in natural waters. *Applied Geochemistry*. 17, 517-568.
- Sparks, D.L., 1995. *Arsenic. An environmental problem limited by solubility* *Environmental Soil Chemistry*, Academic Press, San Diego., pp1-167.
- Su, C. & Puls, W.R., 2001. *Arsenate and Arsenite Removal by Zerovalent Iron: Kinetics, Redox Transformation, and Implications for in situ groundwater remediation*. *Environ. Sci. Technol.* 35, 1487-1492
- Tanabe, K., 1981. *Catalysis—Science and Technology*; Anderson, J.R. and Boudart, M. (eds.); Springer-Verlag, New York. pp. 231-265.
- Tanaka, T., 1988. *Arsenic(III) and Arsenic(V) Adsorption on Three California Soils* *Appl. Organomet. Chem.*, 2, 283-295.
- Theocharis, C.R., Jacob, K.J. & Gray, A.C., 1988. Enhancement of Lewis acidity in layer aluminosilicates. *Treatment with acetic acid*. *J. Chem. Soc., Faraday Trans. 1*(84), 1509-1515.
- Thompson, G.R. & Hower, J., 1975. *The mineralogy of glauconite*. *Clays and Clay Min.*, 23, 289-300.
- Tokunaga, S., Wasay, S.A. & Park, S.W, 1997. Removal of arsenic (V) ion from aqueous solutions by Lanthanum compounds. *Water Science Technology*. 35(7), 71-78.
- Van Olphen, 1977. *Clay colloid chemistry*, Second Edition, Krieger published Company, Malabar, Florida, 318 p.
- Vicente, M.A., Suárez, M., Bañares Muñoz, M.A., López González, J.D., 1996. Comparative FT-IR study of the removal of octahedral cations and structural modifications during acid treatment of several silicates. *Spectrochimica Acta A* 52, 1685-1694.
- Volzone, C., Thompson, J.G., Melnitchenko, A., Ortega, J. & Palethorpe, S.R., 1999. Selective gas adsorption by amorphous clay mineral derivative. *Clays Clay Miner.* 5, 647-657.
- Wilkie, J.A. & Hering, J.G., 1996. Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. *Colloids Surfaces A: Physicochemical and Engineering Aspects*, 107, 97-110.
- William, M., 2001. Mobility of arsenic in saturated, laboratory test sediments under varying pH conditions. *Environ. Geol.* 40, 267-278.
- Wilson M.J., 1999. *The origin and formation of clay minerals in soils: past, present and future perspectives*. *Clay Minerals*, 34, 7-25.
- World Health Organization, WHO, 2001. *Arsenic and arsenic compounds*. *Environmental Health Criteria*, 2nd edition. Geneva, Switzerland. 512 p.
- Worrl, W.E., 1968. *Textbook of Clays: Their Nature, Origin and General Properties* [M]. Macharen and Sons, London. 41p.
- Yavuz, O., Altunkaynak, Y. & Guzel, F., 2003. Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. *Water Res.*, 37, 948-952.

Received at: 05. 12. 2012

Revised at: 22. 01. 2013

Accepted for publication at: 24. 01. 2013

Published online: 25. 01. 2013