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The Removal and Recovery of Arsenic (III) from Aqueous Solution using an Adsorption Process onto Raw-clay

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Abstract

Arsenic (III) is considered among the most dangerous metalloid because of its instability and difficulties to remove it. In this study, we suggest a raw-clay as the adsorbent and we are particularly interested in investigating the equilibrium related to the kinetics and thermodynamics of the removal it from water. CEC, BET and Zeta potential measurements were used in this investigation to explain the metal removal behavior of the adsorbent. The empirically determined sorption kinetics were well fitted to a pseudo-second order model isotherm, while equilibrium sorption data for Arsenic (III) onto the present adsorbent were consistent with the Langmuir model. The maximum amount of adsorption of Arsenic (III) in the raw-clay was 7.19 mg.g^{-1}. An important point concerning the regeneration of the adsorbent was also discussed. Indeed, strong acids appear to be the best desorption agents to desorb arsenic. The use of "aqua regia" gave a rate of adsorbed arsenic desorption close to 97%.

1. Introduction

Arsenic is a metalloid belonging to the same family of nitrogen and phosphorus and to column V in the periodic table. Its name comes from the Greek Arsenikon, which means yellow pigment and it was discovered by Albert Magnus in 1250 [1]. Two forms, arsenite As(III) and arsenate As(V), that are commonly found in natural water [2, 3]. In groundwater, As(III) exists as $H_3AsO_3^-$, H_2AsO^{3-}, and $HAsO_3^{2-}$, which is difficult to be adsorbed onto mineral surfaces [4]. In comparison, the As(V) present as oxyanions H_3AsO_4, H_2AsO^{4-} and $HAsO_4^{2-}$, is adsorbed easily onto solid surfaces. Of both the forms as As(III) is known to be more toxic than As(V) and is predominant in ground waters [2, 5].

Several techniques are used to reduce the concentrations of arsenic in water, in particular coagulation process, reverse osmosis, and adsorption. However, to treat water loaded with metal ions such as aluminum by coagulation [6] is an expensive operation. It is the same using the reverse osmosis requires the use of membranes, which are expensive to maintain and replace, and ion exchange uses costly resins [7]. All of these techniques require the treatment of a reject stream for the final removal of heavy metal. Currently, the adsorption process is used for the removal of trace metals from waste solutions [8] and it is the most widely for removing arsenic because it is simple to apply. Furthermore, raw-clay are the most widely used adsorbents due to their availability and low cost and also due to the existence of different types of active sites on their surface, which include acid sites and ion exchange sites [8]. Based on the neutral pH, many types of natural sorbents were identified in table 1as kaolinite, bentonite [9–17]. Smectite has a negative charge which is responsible for giving superior activity in comparison with other raw-clays as kaolinite [18].

In the present study, a Moroccan raw-clay was used as adsorbents of As(III). The choice of this type of adsorbent is also based on its availability, its relatively lower cost, high surface area, high chemical stability, high sorption properties and rich intercalation chemistry. In addition to all these criteria, raw-clay is an ecological material. So we are particularly interested in investigating the equilibrium related to the kinetic thermodynamics of adsorption to provide a method of attachment and subsequently regenerating the As(III) absorbed onto these natural solids for various reuses.

Table 1. Comparative evaluation of various low-cost adsorbents for As(III) removal.

Adsorbent	pH	Conc. Range/($mg.L^{-1}$)	S_{BET}/($m^2.g^{-1}$)	T/°C	Conc. removal/ ($mg.g^{-1}$)	Ref.
Activated alumina grains	7.00	0.79- 4.90	116- 118	25	3.48	*Lin et al. 2001* [9]
Modified iron oxide-coated sand	7.2	0.5- 3.5	2.9- 7.9	50	0.14	*Vaishya et al. 2002* [10]
$FePO_4$ (amorphous)	7- 9	0.5- 100	53.6	20	21	*Lenoble et al. 2005* [11]
Modified calcined Bauxite	6- 8	0.5- 8.0	-	25	1.37	*Ayoob et al. 2007*[12]
Fresh biomass	6.0	50- 2500	-	30	128.1	*Kamala et al. 2005*[13]
GAC	7.0	1	1.065	20-23	0.09	*Reed et al. 2000* [14]
Activated carbons	7.0	5- 20	1030	25	1.393	*Budinova et al. 2006* [15]
Activated carbons	6.4- 7.5	0.193- 0.992	36.48	25	89.0	*Pattanayak et al. 2000* [16]

2. Materials and Experimental

Materials

The chemical reagents used in this study are $NaAsO_2$ (98%), HCl (37%) and NaOH (99%) and were reagent grade obtained from Sigma Aldrich Company (USA).

The material used as adsorbent was collected in the central area of Morocco and its denomination, “raw-clay” is justified by the fact that it’s commonly employed in the ceramic industries because of its substantial proportion of clay (>40%).

Thus, the chemical composition was done by the ICP-AES. This equipment is a model ICAP 6300 SERIES THERMO with a Spectrometer Echelle type 52.91 grooves/mm ruled grating 383 mm effective focal length 9.5° UV fused silica cross dispersion prism. Its Detector is High performance CID86 chip, RF source 27.12 MHz solid state 750-1500 watts output power (Duo restricted to 1350 watts). The samples proposed for the analyzes were subjected beforehand to the action of aqua-regia (mixture of HCl and HNO_3) by microwaves according to a defined program and the analysis of all the elements is made by standards of 1000 mg/L obtained from Sigma Aldrich Company. The results of this analysis are given in table 2. The extract is then filtered and adjusted to volume with nitric acid. The uncertainty on the measurement of the concentration of Arsenic by ICP-OES was 0.01 whereas for the major elements (Na, K, P, Mg, S, Ca, Si and Al) was 5 and for Fe, Cu, Mn and Zn was 0.1.

Table 2. The parameters of the analysis by ICP.

	CuO %	ZnO %	CaO %	K_2O %	MgO %	Na_2O %	P_2O_5 %	SO_3 %	Al_2O_3 %	Fe_2O_3 %	MnO %	SiO_2 %	**As/ *(mg/kg)***
A	0.01	0.02	2.10	0.18	1.57	0.80	0.12	0.75	11.44	4.29	0.09	59.32	**2.19**
B	0.01	0.02	2.18	0.17	1.57	1.38	0.12	0.75	11.73	4.34	0.09	59.32	**1425**
C	0.01	0.02	2.14	0.19	1.57	0.80	0.12	0.75	11.43	4.30	0.09	59.32	**43.53**

The elemental analyses determined by ICP before adsorption is shown in Table 3 line A. The results show that the raw-clay is relatively rich in silica, calcium and iron oxide. It includes a large amount of Muscovite which is similar to illite [19]. The content, relatively important in magnesium (Mg), is probably due to the presence of a double carbonate and/or to the substitution of the ion Al^{+3} by the ion Mg^{+2} in the octahedral sites of the raw-clay minerals. The SiO_2/Al_2O_3 ratio exceeds 3 which confirms the presence of smectites. We note that the structure of this material contains a very small amount of As(III) (2.19 $mg.kg^{-1}$). These comments can be confirmed by the X-ray diffraction which allows identifying the main minerals present in this sample (Fig.1A).

On the other hand, the raw material is dried in an oven at 110°C for 24h and it is then crushed and sieved in a chopper sifter. The raw-clay was also characterized by powder x-ray diffraction (XRD) using a Phillips Xpert-pro diffractometer bruker D8 advanced. Copper Kα radiation (λ=1.5406) producted at 50KV and 20mA. Diffractograms were recorded from 5 to 85° (2θ) with a step size of 0.02° and a count time of 5s per step.

The analysis by X-ray diffraction of the raw-clay showed that it is formed mainly of associated minerals and calcite, with traces of hematite and dolomite (Fig.1A). The characteristic lines of Muscovite have been detected towards reflection peaks that occur at 2θ=42.5°. Small reflections at 2θ=31.5° and 50° can also be attributed to the presence of calcite. The presence of dolomite and quartz has been confirmed by the presence of reflections at 2θ=37° and 55° for dolomite and at 2θ=21°, 27°, 60°and 70° for quartz.

Regarding the specific surface area of this solid, it was determined according to the Brunauer–Emmet-Teller (BET) equation with nitrogen adsorption isotherms at 77 K using a Multi-point Beckman Coulter Surface Analyzer SA 3100. The high value of the specific area (287 $m^2.g^{-1}$) is coherent with the presence of smectite. The cation exchange capacity (CEC) was measured by the hexamino-cobalt method as described elsewhere [20]. The high value of CEC (95meq/100g) confirms that the raw-clay contains smectite and was coherent with the mineralogical composition. The Zeta potential was achieved using the device Malvern zetameter model Zetasizer Nano Z. The negative value measured, shown that the mineral have a negative charge which can be influenced by parameters such as pH and ionic strength.

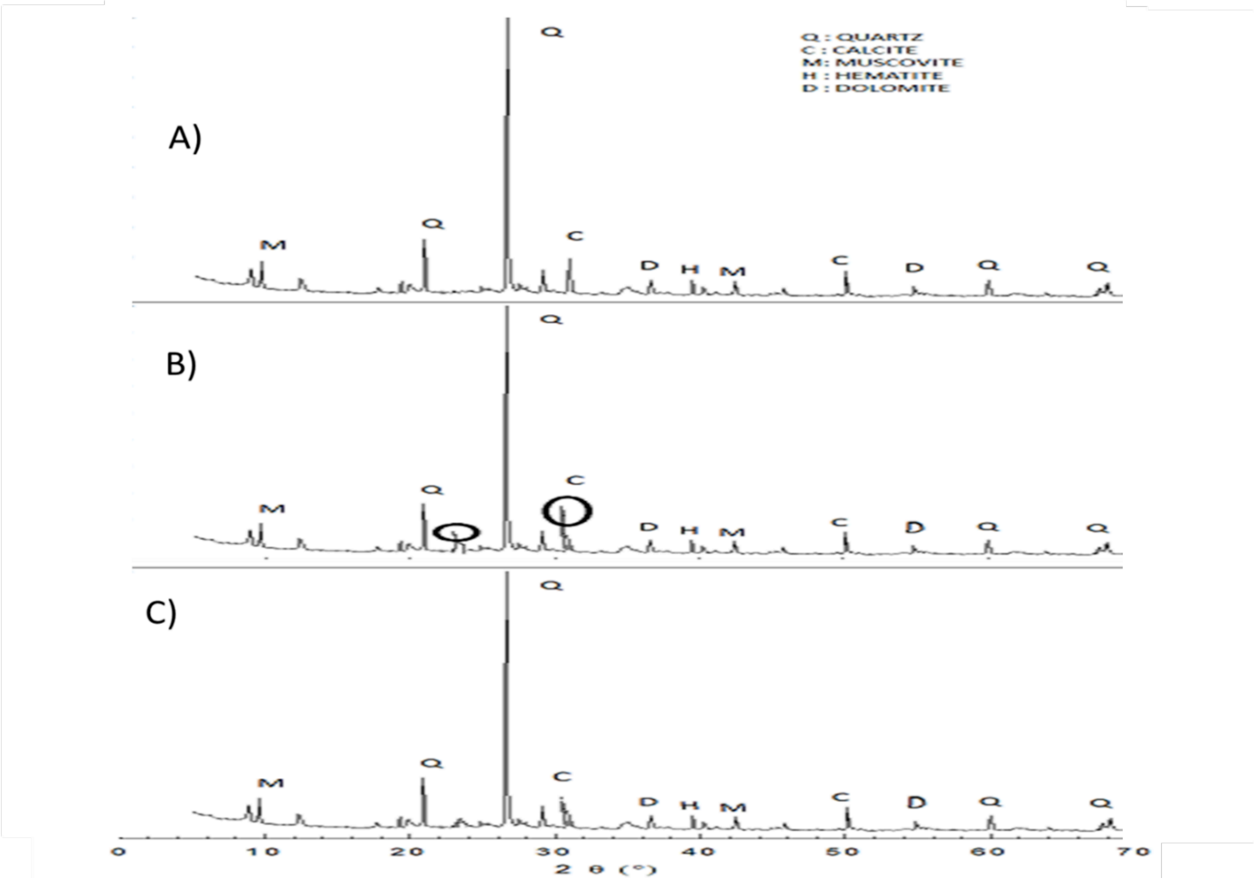

Fig. 1. The XRD pattern of the clay before adsorption (A), After adsorption (B), After regeneration (C)

3. Experimental

In order to carry out the tests of adsorption, various solutions of As(III) with a concentration of 5, 10, 15, 20, 25, 30, 35, 45 and 50 mg.L^{-1}were prepared by dissolving $NaAsO_2$ in ultrapure water (grade1). As(III) adsorption was investigated by stirring 0.2 g of the raw-clay in 50 mL of solution as described previously [21]**.** The pH of the solution was controlled and fixed at 7 during the experiments. The equilibrium experiments were performed for 3 h at a temperature of 298K with a rotation of 300 rpm. After 3 h, the supernatant solution was separated from the solution by centrifugation and left in the oven while the solution was analyzed by ICP for the purpose to detecting the presence or absence of arsenic ions. At first, the effect of initial concentration of As(III) on the amount adsorbed by raw-clay was studied using 0.2 g of the adsorbent and 50 ml of As(III) solution with a contact time of 180 minutes. As(III) solutions varied from 5 to 50mg.L^{-1} with constant temperature (25°C) and pH set at 7. Tests of adsorption were carried out as described previously and the calculation of the adsorbed quantity on the sample is obtained by the relationship;

$$Q_e = \frac{(C_0 - C_e).V}{m} \qquad \textbf{(Eq.1)}$$

Where Q_e is the quantity adsorbed (mg.g^{-1}), m is the mass of the adsorbent, C_0 is the initial concentration of the solute (mg.L^{-1}), C_e is the concentration at equilibrium (mg.L^{-1}) and V is the volume of the solution (50 mL). The concentration of arsenic has been determined by ICP-OES.

In order to study the effect of pH, the tests have been achieved by agitation of 50 mL of a solution of arsenic (40mg.L^{-1}) with 0.2g of the sample for 3 hours at 25°C. The pH of the solutions has been adjusted on the following values; 2; 4; 6, 8; 10 and 12 by adding a few drops of concentrated solutions of HNO_3 or NaOH (0.1 M).

The evolution of adsorption process as a function of time was studied using 0.2g of the adsorbent mixed with 50 mL of a solution of As(III) from initial concentration of 40mg.L^{-1}during 5 hours with a levy on each 30 min after centrifugation and filtration.

The regeneration of the adsorbent

To retrieve the arsenic adsorbed and regenerate later, which is the most difficult step and less studied in literature, it was decided to recover the arsenic by attacking the solid with its adsorb by different acids at various concentrations. This process was carried out by adding 0.2 g of raw-clay containing arsenic in 50mL of different acids including the nitric acid (2M), the hydrochloric acid (2M), the aqua regia (75% HCl, 25%HNO_3), the sulfuric acid (2M) and finally the hydrogen peroxide H_2O_2. These mixtures are shaken for 3 hours in a shaken water bath (300 rpm) before the filter to analyze these solutions by ICP-OES.

4. Results and Discussion

Characterization of the sample before and after adsorption

In order to test qualitatively the ability of this material to remove arsenic, we conducted preliminary experiments of adsorption from aqueous solution and we analyzed the solids. The elemental analyses determined by ICP *before adsorption and after adsorption* are shown in Table 3 (Lines A and B). We note that the structure of the raw material initially contains a very small amount of As(III) (2.19 mg.kg^{-1}). The chemical composition *after adsorption* has not changed which we observe the dominance of the silica, calcium, iron oxide, the presence of alumina, the content relatively important in magnesium. However the increase of As(III) content of the sample gives us an idea of the efficiency of the adsorption. This content was markedly increased after the adsorption. The analysis by X-ray diffraction of the raw-clay showed that As(III) was not detected before adsorption, whereas the spectrum of the material after adsorption showed a peak relative to the attachment of As(III) at 2θ=31° (Fig. 1B). This result is confirmed by the IR (Fig.2).

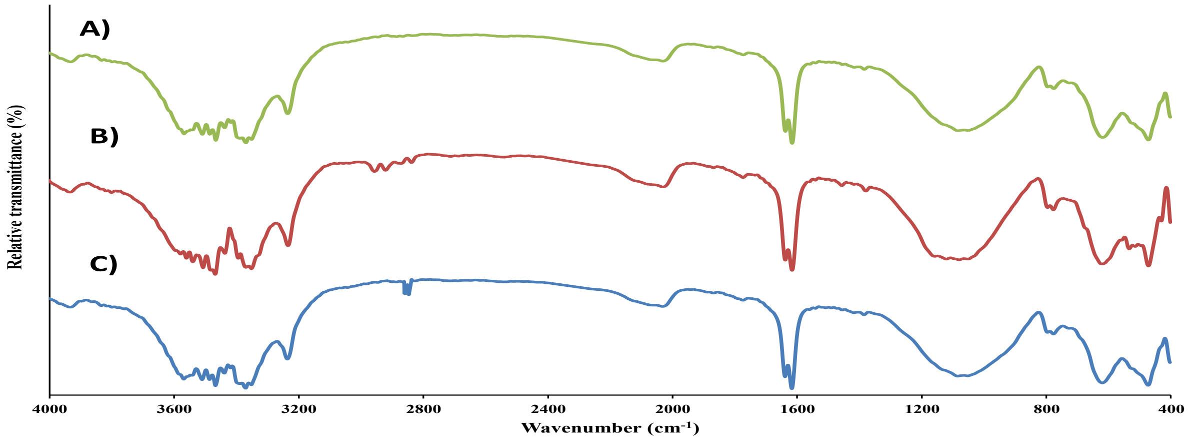

Fig. 2. Infrared spectra ofthe geomaterial before adsorption (A), After adsorption (B),After regeneration (C)

IR spectra were recorded on a Bruker Vertex-70 FT-IR spectrophotometer. Effectively the IR spectrum of the raw-clay (fig.2A), shows Al−OH and O−H stretching at 3584 cm^{-1}, hydrogenbonded water H−O−H stretching at 3450 cm^{-1}, H−O−H deformation in 1673 cm^{-1}, Si−O−Si stretching in 1050 cm^{-1}, and Si−O deformation at 750 cm^{-1}. However, spectrum of the solid after adsorption reveals a peek at 2850 cm^{-1} assigned to the arsenic (Fig.2B) [22].

Results of effect of As(III) initial concentration, pH and Kinetics study

Experimental data from the adsorption of As(III) by raw-clay as a function of the initial As(III) concentration was presented in Fig.3. As expected, increasing the initial As(III) concentration resulted in decreasing percent removal. This study gave an optimal initial concentration equal to 40mg.L^{-1} (8.45mg/kg) as adsorbed which will be the initial concentration of the rest of experiments.

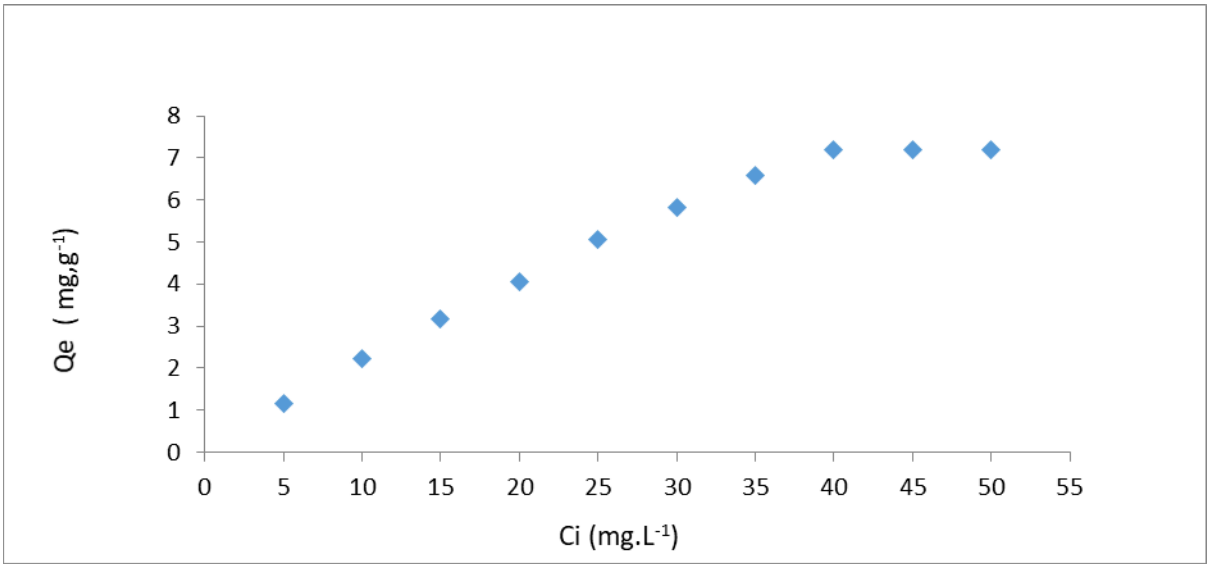

Fig. 3. The effect of initial concentration on As (III) adsorption in 0.2g of adsorbent for 3 hours and at pH=7

The pH effect on the amount of As(III) adsorbed onto the raw-clay was studied by varying the pH from 2 to 12. The Figure 4 showed that the performance of adsorption was increased in the range of pH between 2 and 6 corresponding to 7.19 mg.g^{-1} of As(III) fixed by the solid, and begins to decline in pH values above 8 (5.41 mg.g^{-1}). We therefore deduce that the availability of arsenic sites depends on the pH. The optimum of pH for the removal of arsenic by adsorption on the raw-clay was pH 6. This result is comparable with others studies which have confirmed that the optimum pH for adsorption of arsenic on different adsorbents is an approximately neutral pH [22–26]. These results showed that the most frequent form of As(III) in an acid medium is most likely $H_3AsO_3^-$, the As(III) adsorption is favorable. This is due to the strong interaction that occurs between the adsorbent and $H_3AsO_3^-$. At a pH above 8, the absorbent surfaces become negatively charged. Therefore, the interaction between the adsorbent and the arsenite ions decrease [27].

The study of the adsorption kinetics is necessary for the determination of the equilibrium time between the solute and the adsorbent and it's necessary to investigate the intraparticle diffusion. The performance of the reaction for adsorption of As(III) on the raw-clay as a function adsorption's time was studied in the range of time between 30 and 300 min. The Figure 5 shows that the adsorption increases with contact time up to 180 min. While the contact time exceeds this limit, the adsorption of the whole As(III) process seems to be limited by the fact that the adsorption process in origin depends on the reaction between As(III) species and the active sites available.

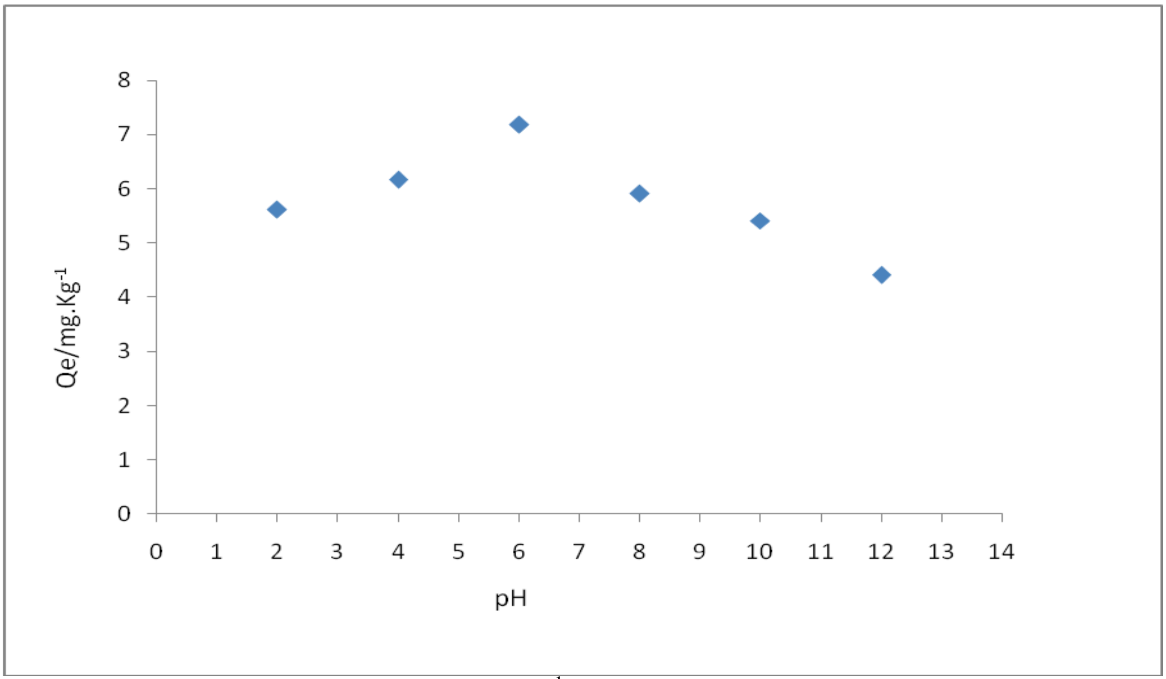

Fig. 4. The effect of pH on As(40 mg.L^{-1}) adsorption in 0.2g of adsorbent for 3 hours

The order of the reaction is a very important parameter in the determination of reaction mechanisms. The orders concerning the adsorption on the raw-clay the most cited in the literature are;
i) The pseudo-first order expressed by the equation of Lagergren [30];

$$Ln(Q_e - Q_t) = LnQ_e - K_{ads}.t \quad \textbf{(Eq.2)}$$

The graph of $ln(Q_e\text{-}Q_t)$ *vs t* is a right of the equation with the slope equal to K_{ads} and ordered to the origin equal to lnQ_e (Fig.6). Where Q_t is the amount adsorbed at the moment t (mg.g^{-1}); Q_e is the amount adsorbed to the equilibrium (mg.g^{-1}) and k_{ads} is the rate constant of adsorption of pseudo-first order (min^{-1}).
(ii) The Pseudo-second order expressed by the equation (3) [31];

$$\frac{t}{Q_t} = \frac{1}{K_{ads}.Q_e^2} + \frac{1}{Q_e} \quad \textbf{(Eq.3)}$$

The right of $\frac{t}{Q_t}$ *vs t* (Fig.7) can give the slope $\frac{1}{Q_e}$ and ordered to the origin $\frac{1}{K_{ads}.Q_e^2}$.
The values of the constants of pseudo-first and second order and the regression coefficients R^2 are compared with other studies in Table 5. From the analysis of these results, a good correlation of the experimental points ($R^2=0.997$) has justified. Which means that the kinetics of adsorption of As(III) on the sample follows the second order with a constant value of adsorption k_{ads} equal to 19.377 g.mg^{-1}.min^{-1}. This result implies that the “reaction” between arsenic and raw-clay is controlled by the diffusion. This same result is found in several other studies, which confirmed that adsorption of arsenic on an inorganic material follows the second order model. Except that the equilibrium of our adsorption is reached quickly (3 hours) compared to other studies whose adsorption is very slow and that can happen more than 30 hours with amount of experimental adsorption of As(III) more six folds than other works [24, 27, 32, 33]. Some authors deduce that the sorption process might be chemisorption. In our opinion, this, it cannot be justified by the current parameters of adsorption, it is essential to determine quantities of direct adsorption heats using calorimetry of adsorption. In the present case, the pseudo-second-order model is well describing the reaction kinetics [34].

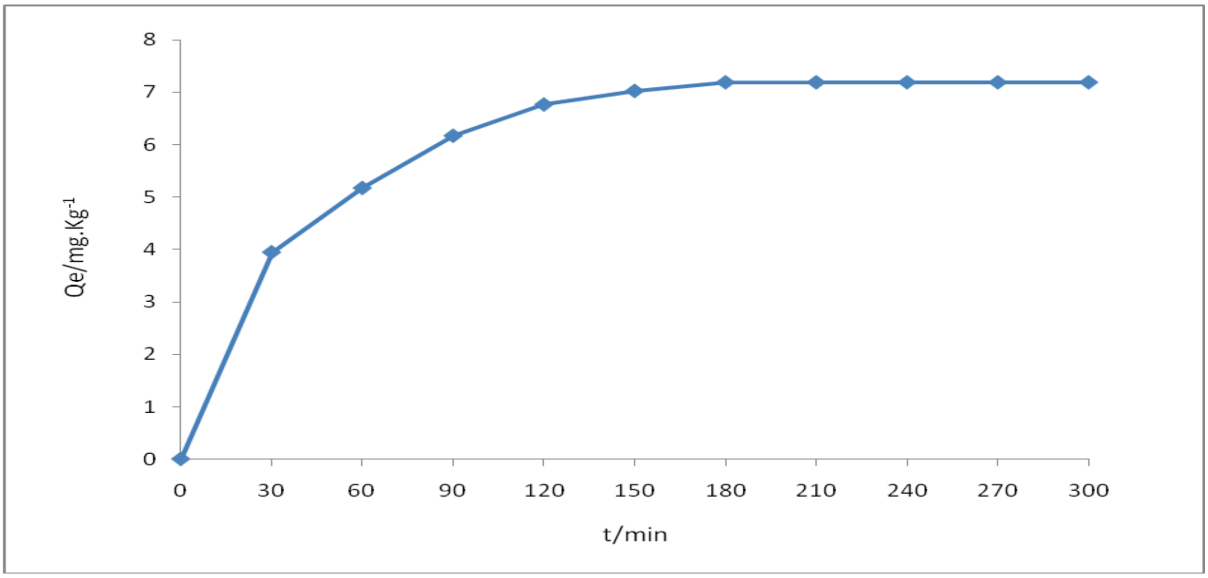

Fig. 5. Time effect on the performance of the adsorption of 40 mg•L^{-1}As (III) on 0.2g of adsorbent at pH = 6

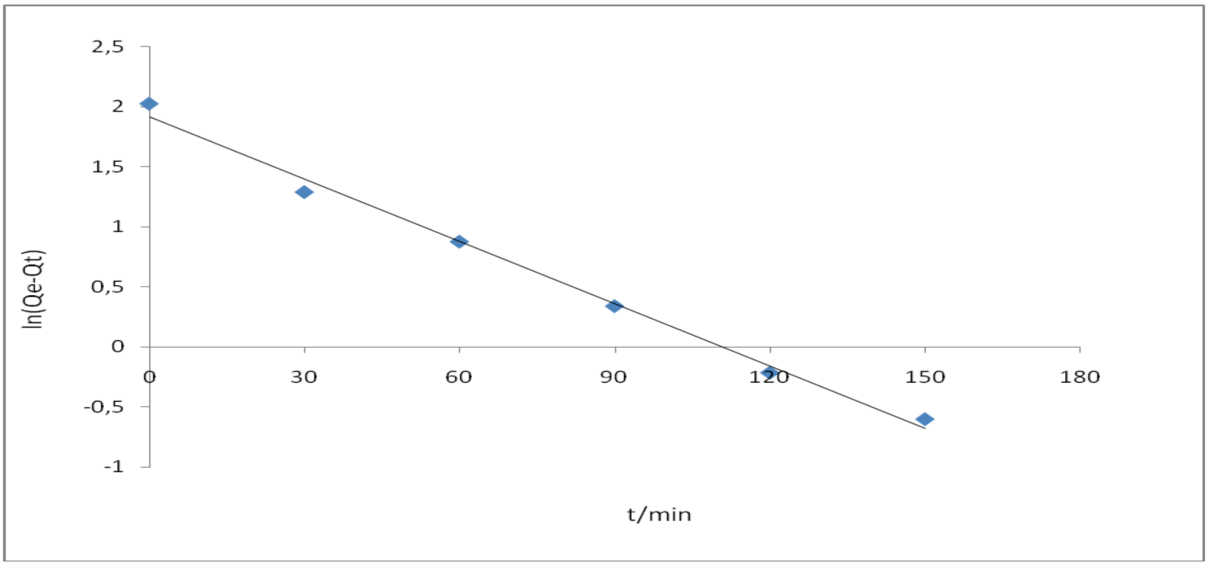

Fig. 6. The pseudo-first-order

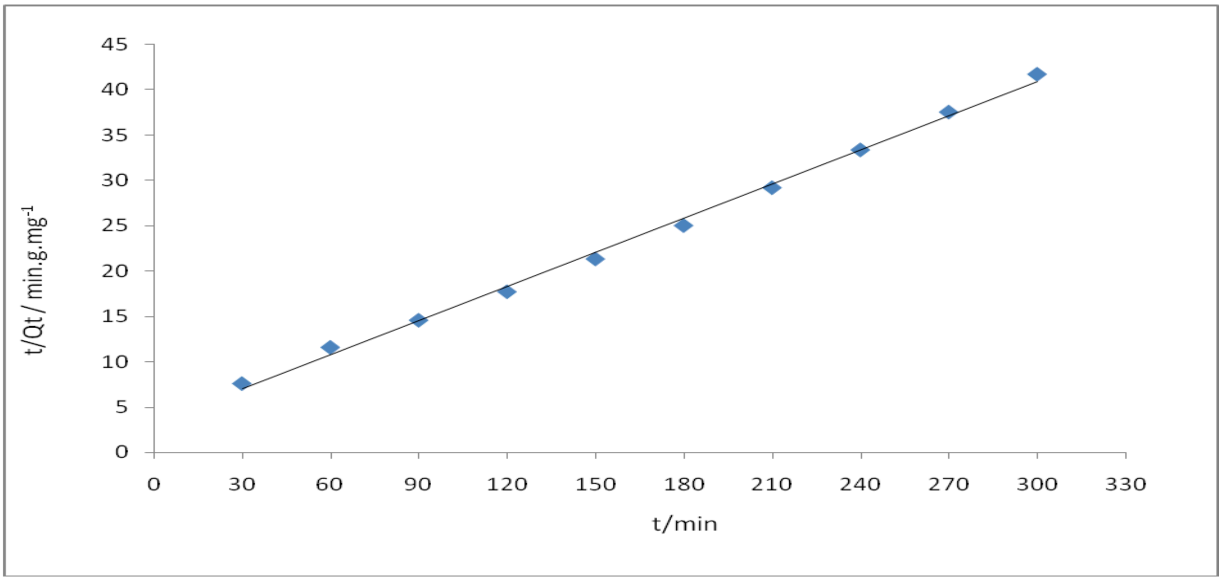

Fig. 7. The pseudo-second-order

Table 3. The kinetic parameters of the adsorption of As (III).

First-Order-Model			**Second-Order-Model**			**Experimental**	**Ref.**
$Q_{e,cal}$/ ($mg.g^{-1}$)	K_{ad}/ (min^{-1})	R^2	$Q_{e,cal}$/ ($mg.g^{-1}$)	K_{ads}/ ($g.mg^{-1}\ min^{-1}$)	R^2	Q_{exp}/ ($mg.g^{-1}$)	
4.33	0.0196	0.770	0.0115	10.77	0.990		*Ho et al. 1998* [31]
1.23	0.0003	0.956	2.06	0.00004	0.999	1.94	*Anjum et al. 2011* [27]
	0.0227		0.2054	0.8924	0.990	0.1984	*Ayoob et al. 2007* [12]
6.80	0.0173	0.9931	7.97	19.377	0,997	7.1925	This study

Proposed Mechanism

The term "sorption" usually defines the change in concentrations of chemical constituents in the solid phase as a result of mass transfer between solution and solid, and thus sorption includes various types of removal mechanisms such as absorption and ion exchange. Fig.4 showed the distribution of arsenic species (V) as a function of pH. The As(III) in solution above pH 6 is present in an ionic form $H_3AsO_3^-$ and therefore can be effectively removed by hydroxide attached to the surface of the sample. Whereas in the pH intervals 7-9 only a small percentage of $H_3AsO_3^-$ is dissociated. Raw-clays are generally characterized by the presence of three active sites located at the edge of the leaves, the two hydroxyl groups of surface which are silanol groups, aluminol groups and Lewis acids [28]. The aluminol groups are the most favorable sites for the adsorption of anions significant presence of oxygen atoms relative to silanol sites. In an acid environment, these sites are characterized by a presence of functional groups charged positively ($AlOH_2^+$) allowing the retention of arsenic in the form of $H_3AsO_3^-$. On the other hand, in a basic medium, the charge of these sites becomes negative, which causes electrostatic repulsion between these sites. This theory is in agreement with the results cited by Huang [29] who had studied the adsorption of arsenic by bentonite and vermiculite. He pointed out that arsenic adsorbs mainly on aluminum oxide from the outer surface of this raw-clay. Arsenic can also be attached indirectly to aluminol sites via solution cations which can be adhered to aluminol sites and provide an additional positive charge thus promoting the adsorption of arsenic. Thus for effective treatment of As(III) the solution pH should be about 6.

Sorption isotherms

The modeling of the adsorption isotherms is made by using the Langmuir and Freundlich isotherm.

Langmuir isotherm model

The Langmuir isotherm in liquid phase is given by the relationship [35] ;

$$Q_e = \frac{Q_m.K_L.C_e}{1+K_L.C_e} \qquad \textbf{(Eq.4)}$$

This equation has been treated in its linearized form called Langmuir 1;

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L.Q_m} \qquad \textbf{(Eq.5)}$$

With Q_e is the adsorption amount of arsenic in the equilibrium (mg.g^{-1}) ; Q_m is the maximum capacity of adsorption of arsenic (mg.g^{-1}); K_L is the equilibrium constant of adsorption named constant of Langmuir (L.g^{-1}); C_e is the concentration of the solute at the equilibrium (mg.L^{-1}). In carrying $\frac{1}{Q_e}\ vs\ \frac{1}{C_e}$, the Langmuir equation linearized allows the determination of two important parameters of the adsorption, namely the ultimate capacity of adsorption, Q_m and the equilibrium constant of adsorption, K_L, from the ordered to the origin and the slope, respectively.

Freundlich isotherm model

The Freundlich isotherm is the mathematical descriptions that is usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression of the surface state, the exponential distribution and the energies of the active sites. It describes theoretically a heterogeneous system and a reversible adsorption process that is not limited to the formation of monolayers as the Langmuir model. The Freundlich equation is as follows [36] ;

$$Q_e = K_f . C_e^{1/n} \quad \textbf{(Eq.6)}$$

With Q_e is the adsorption amount of arsenic in the equilibrium (mg.g^{-1}) and C_e is the concentration of the solute at the equilibrium (mg.L^{-1}).The linear form of the above equation is given as ;

$$LnQ_e = LnK_f + \frac{1}{n} LnC_e \quad \textbf{(Eq.7)}$$

K_f is the Freundlich constant (mg.g^{-1}) and 1/n is the heterogeneity factor. When a plot of LnQ_e *vs* LnC_e gives a straight line the values of K_f and n can be calculated from the intercept and slope of the plots respectively.

Figure 8 and Figure 9 show the results of this modeling. The values of the constants of Langmuir and Freundlich were presented in table 4. By adjusting the experimental points on these models, and based on the values of the coefficient R^2, it appears that the model of Langmuir expresses the type of adsorption ($R^2 = 0.9904$) better than Freundlich ($R^2 = 0.5589$).

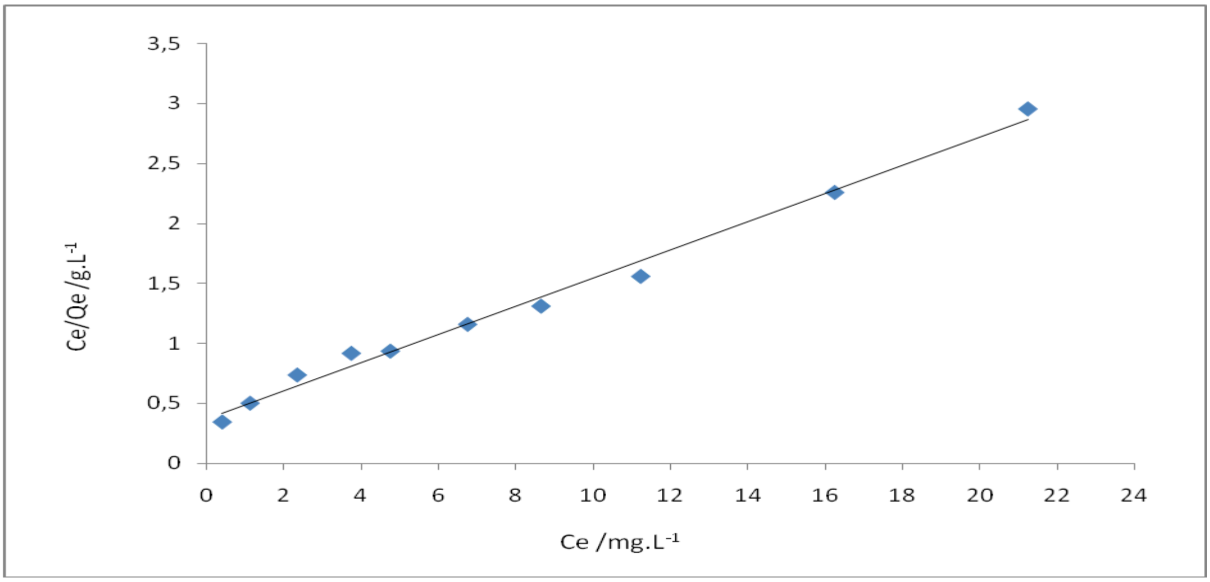

Fig. 8. The model of Langmuir

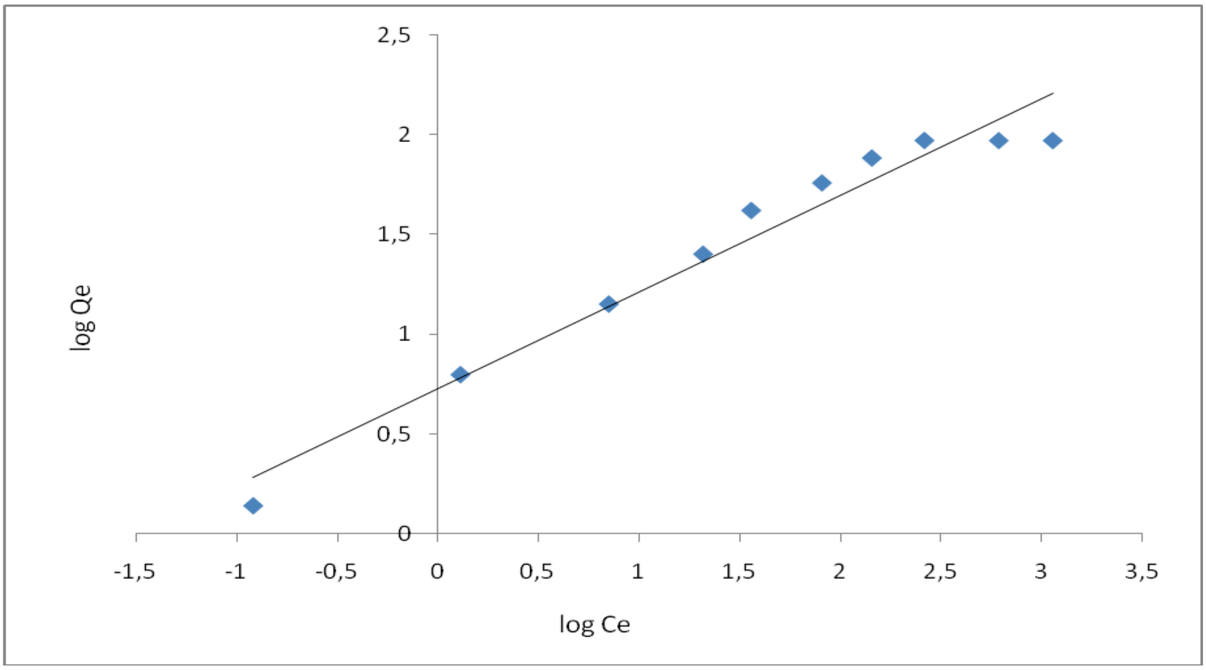

Fig. 9. The Freundlich isotherm

Table 4. Calculated constants for Langmuir and Freundlich isotherms on sorption of arsenic onto geomaterial (25°C, initial pH 6.0).

Model	Parameters	values	Ref.
Langmuir	$Q_{m,cal}/(mg.g^{-1})$	54.2	Qi *et al.* 2015 [39]
		12.5	Liu *et al.* 2015 [26]
		4.19	Bentahar, *et al.* 2016 [24]
		8.503	This work
	$K_L/(L,g^{-1})$	0.456	Qi *et al.* 2015 [39]
		0.021	Liu *et al.* 2015 [26]
		1.36	Bentahar, *et al.* 2016 [24]
		0.3708	This work
	R^2	0.960	Qi *et al.* 2015 [39]
		0.986	Liu *et al.* 2015 [26]
		0.982	Bentahar, *et al.* 2016 [24]
		0,9904	This work
Freundlich	n	2.62	Qi *et al.* 2015 [39]
		0.52	Bentahar, *et al.* 2016 [24]
		2.06	This work
	$K_F/(mg^{1-1/n}.L^{1/n}.g^{-1})$	48.82	Qi *et al.* 2015 [39]
		2.40	Bentahar, *et al.* 2016 [24]
		5.35	This work
	R^2	0.985	Qi *et al.* 2015 [39]
		0.986	Bentahar, *et al.* 2016 [24]
		0.5589	This work

As well, the molecules of the arsenic could be adsorbed in monolayers, without the arsenic-arsenic interactions. These results are in agreement with those in literature. Most work studying the adsorption of arsenic found the appropriate model for this phenomenon is the Langmuir model with a low correlation coefficient (0.97) and a maximum adsorption capacity of 0.561 $mg.g^{-1}$ [24]. According to the literature, the correlation with the model of Langmuir [37, 38] assumes that each site of the sample can only be occupied by a molecule. The formation of a monomolecular layer on the surface of the sample and all sites of adsorption are equivalent and therefore iso energetic. Indeed interactions among the adsorbed molecules on the surface are negligible [35].

The regeneration of the adsorbate

In most of the arsenic sorption studies discussed earlier, desorption/regeneration was not widely discussed. The regeneration of the adsorbed metals is an important consideration for the treatment and recovery of these metals in a concentrated form with a low cost. In this work tests of the regeneration of the adsorbed arsenic using different acids are presented in the Table 5. The results show that aqua regia acid is more compatible to retrieve the adsorbed arsenic since it gives a performance of 96.66% while the nitric and hydrochloric acid which each one gives a performance of respectively 89.29% and 93%. The hydrogen peroxide H_2O_2 has no effect on the adsorbent containing arsenic adsorbed which can confirm again that we were able to make it enter the arsenic in the interlayer space of the sample. The characterization and analysis of the sample *after regeneration* by ICP was presented in table 3, line C. We noted again that silicon oxide (59%) and aluminum oxide (11%) are the major oxides in our material which possess the highest content of silicon oxide due to the large presence of the free quartz. The iron oxide content in the sample was superior to 2%. Calcium oxides exist in the high content. In fact the quantity of arsenic present in the solid decreases after the regeneration which gives value to this process (Table 2). As expected according to XRD data from Fig. 1 (C), the peak related to arsenic is present but in less intensity. On the other hand, Using the Analysis by FTIR, Fig. 2 (C) showed that sample after regeneration contains a low amount of As(III). Other studies have not been able to recover arsenic adsorbed because of the oxidation of arsenic (III) by the manganese present in the Blast Furnace Slag used as adsorbents to remove arsenic from industrial water [21], Sigdel *et al.* have recovered just 56.6% of the arsenic adsorbed onto hydrous iron oxide-impregnated alginate beads [22]. In addition, just 83% of the arsenic removed by Fe-Mn oxide binary chitosan impregnated beads [39]. To our knowledge, this is the first time that recovery performance of arsenic has reached 97%.

Table 5. The regeneration of the adsorbed arsenic.

Acid	Blanc (As) / *(mg/L)*	As final concentration / *(mg/L)*	Yield (%)
HCl	0,25	33.5	93
HNO_3	0,13	32.12	89.29
H_2SO_4	0,08	28.19	78.30
Aqua regia	0,27	34.8	96.66
H_2O_2	0	6,13	6,39

Conclusion

The first objective of this study is to assess the performance of the adsorption of arsenic (III) onto a raw-clay used in different areas. The second objective is to recover the adsorbed arsenic to be reused again. The results obtained indicate that the maximum of As(III) uptake on raw-clay is 7.19 mg.g^{-1} (71.93%). The kinetics of As(III) adsorption on raw-clay used is well described by a pseudo-second-order chemical reaction model, which indicates that the adsorption process of these species is "likely" to be chemisorption. The adsorption isotherms are indicative of monolayer adsorption from the experimental data fit better to Langmuir isotherms. The removal of As(III) is pH-dependent and an optimal adsorption of arsenic is obtained at pH 6. This investigation was supplemented by the regeneration of arsenic by washing the solid after adsorption with aqua regia with a recovery of 96.66 %. Raw-clay exhibits a satisfactory performance for adsorption of As(III) from aqueous solution. The optimum conditions for adsorption were 40 mg.L^{-1} for the initial concentration, pH ≤ 6 and 180 min for the contact time.

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