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# Arsenic removal from aqueous solutions and the impact of humic and fulvic acids



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#### ABSTRACT

This work studied the impact of humic and fulvic acids on the removal kinetics of arsenic (V) by granular ferric hydroxide (GFH) and the adsorption capacity of arsenic (V) onto GFH at equilibrium. The Freundlich and DubininRadushkevich models describe the arsenic (V) adsorption behavior onto GFH reasonably well ( $r^2 > 0.905$ ). The removal kinetics were studied by fitting the experimental data to both first-order and second-order models. The lowest adsorption capacity was observed in the presence of fulvic acids (FA), and conversely, the adsorption capacity in the presence of humic acids (HA) was lower than that without humic substances (WHS). The removal kinetics of arsenic (V) were well defined for the second-order model, with correlation coefficients ranging from 0.951 to 0.977. This study suggests that the presence of humic substances negatively impacts the removal of arsenic from water.

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#### 1. Introduction

The presence of arsenic in natural water is a worldwide problem due to anthropogenic activities Wang and Mulligan (2006) as well as to its high toxicity and carcinogenicity Smith et al. (1992). The principal source of dissolved arsenic in groundwater is often the mobilization of natural deposits in rocks, sediments, and soil. Another important source of arsenic in groundwater is the reductive dissolution of arsenic-bearing iron and other oxyhydroxides (Camacho et al. (2011)). In addition, discharged industrial waste containing arsenic is an important anthropogenic contribution to pollution in continents such as Asia (Mukherjee et al. (2006))or regions such as Mexico (Armienta and Segovia (2008)).

The World Health Organization Organization (2004) has reduced the guideline value for arsenic in drinking water from 50 to 10  $\mu g \ L^{-1}$  to reduce health problems associated with arsenic in natural water. The Health Minister (SAA) of Mexico has implemented a new maximum contaminant level of 25  $\mu g \ L^{-1}$  for arsenic in drinking water (Norm (2000)). These arsenic standards will lead to changes in infrastructure to upgrade existing water treatment

systems and develop new treatment options, for example, removal of arsenic by coagulation with ferric ions and coarse calcite (Song et al. (2006)) or using modified natural zeolite (Baskan and Pala (2011)).

Many different materials appear to be efficient when it comes to remove arsenic from water. For instance, Nieto-Delgado and Rangel-Mendez (2012) demonstrated that the use of granular iron hydro (oxides) as arsenic adsorbent could give an effective approach to increase the adsorption capacity. Actually, they found that materials containing smaller iron hydro(oxide) particles exhibited an enhanced arsenic adsorption capacity. Also, they determined that the best adsorbent material reported an arsenic adsorption capacity of 4.56 mg As  $g^{-1}$  at pH 7. A previous study reported an uptake capacity of 3.7 g  $L^{-1}$  of Arsenic through the use of iron hydroxide granulates (GIH) (Daus et al. (2004)). Tresintsi et al. (2012) reported that the use of iron oxy-hydroxides synthesized in a continuous flow kilogramme-scale production reactor and found that the highest adsorption capacity was shown by the schwertmannite, 13  $\mu$ g As(V) mg<sup>-1</sup>, while maintaining a residual arsenic concentration of 10  $\mu$ g  $L^{-1}$  at an equilibrium pH 7. Another study also demonstrated high affinity between arsenic and metal oxides/hydroxides such as hematite. Magnetite, goethite and iron rich laterite in aqueous solutions (Aredes et al. (2012)). They found that iron rich laterite was the most effective for As removal,

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followed by goethite, magnetite and hematite. Treatment of 100 mL of water containing 20 ppm arsenic with 5 g of laterite reduced the arsenic level down to 10 ppb. Alternatively, Jiang et al. (2012) through the coating of polystyrene by Nano-Fe $_3$  O $_4$  shown that it is possible to obtain adsorption capacities 77.7% greater than that of bulky Fe $_3$  O $_4$ .

The use of composite adsorbents based on chitosan and copper hydroxide  $\text{Cu}(\text{OH})_2$  or copper oxide CuO was proved to be another effective approach as shown by Elwakeel and Guibal (2015). They reported a maximum capacity of 39.0 and 28.1 mg As  $\text{g}^{-1}$  for chitosan/ $\text{Cu}(\text{OH})_2$  and chitosan/CuO, respectively, at 20 °C and equilibrium pH ranging in 5–6. They found a removal efficiency and a metal recovery over 95% for five successive sorption/desorption cycles. In a previous report (Elwakeel (2014)), so as to improve the efficiency of the chitosan, it was cross-linked using glutaraldehyde in the presence of magnetite. The results showed high affinity and fast kinetics for the adsorption of As(V) where an uptake value of 1.30 mmol  $\text{g}^{-1}$  was reported at 25 °C.

The use of zero-valent iron allowed greater Arsenic removals than 95% at laboratory tests and field-columns studies (Lackovic et al. (2000)). Another study suggested that increasing  $Ca^{2+}$  concentration but decreasing  $PO_4^{3-}$  and HA concentrations can create conditions for the best removal of both As (III) and As (V) (Tanboonchuy et al. (2012)). However, it was found that the removal of arsenic in zero-valent iron systems involves complicated processes including surface adsorption and precipitation (Su and Puls (2001)).

Natural organic matter (NOM) is ubiquitously dissolved in aquatic systems, and it is present in groundwater with concentrations ranging from 0.5 to 10 mg  $L^{-1}$  (Genz et al. (2008)). In the presence of NOM, the removal of arsenic by metallic oxyhydroxides is mainly affected by changes in the surface reactivity and properties of the metallic oxy-hydroxides. Additionally, the presence of NOM in water modifies the properties of other contaminants present in the water (properties such as electrophoretic mobility, transport and interactions with other colloids) (Rahman et al. (2013)). Usually NOM is composed of several acidic functional groups, which are dissociated in aqueous solutions, leading to negatively charged macromolecules (Gagnon et al. (1997)). Conversely, when the particles of ferric oxy-hydroxide are dispersed in an aqueous media, the surface charge, which is controlled by the pH and ionic forces in the aqueous solution (Schwertmann and Cornell (2008)), begins to change (Illés and Tombácz (2003)). Surface reactions with the H and OH in FeOOH lead to the formation of charged sites where the negatively charged sites of NOM are able to bind with these positively charged sites on the FeOOH (Rahman et al. (2013)).

Humic substances are mainly classified into the following three fractions: fulvic acids (FA), humic acids (HA), and humin. In fact, it has been found that arsenic forms a slightly more stable associations with FA than those formed with HA at neutral pH (Mandal et al. (2013)). Moreover, it has been found that complexation of arsenic with dissolved organic matter (DOM) plays an important role in regulating As removal and transformation, because of the ubiquitous of DOM in aquatic environments and can interact strongly with As species (Liu and Cai (2010)). The release of As from soils, aquifer materials and sediments into groundwater is controlled by a number of factors (Liu et al. (2013)). Where the main influencing mechanisms include competition of available adsorption sites, formation of aqueous complexes and/or changes in the redox potential of site surfaces and As redox speciation (Reza et al. (2010)). However, it was demonstrated that dissolved organic carbon (DOC) content was also a critical factor in enhancing mobilization of both As(V) and As (III) in soil (Dobran and Zagury (2006)). Correlations between As concentrations and small molecular weight DOM with protein-like peak signatures also showed that biologically degraded sedimentary organic matter infiltrated into shallow aquifer and enhanced the mobilization of As in ground-water (Tareq et al. (2013)). Accordingly, it can be mentioned that organic matter is not only a redox driver, but also one of the sources of As in groundwater (Anawar et al. (2013)). The adsorption of NOM onto mineral surfaces showed that its binding is dependent on the pH and the electrolyte concentration. This binding is not completely understood due to heterogeneity and complexity of NOM and adsorption surfaces as reported by (Buschmann et al. (2006)) and (Redman et al. (2002)).

Accordingly, the aim of the present work is to study the effects of the presence of HA and FA on the removal kinetics of arsenic (V) and its adsorption capacity as well as to provide critical information for the design of GEH filters capable to remove arsenic in realistic conditions found in the zone of Bajio, México. The typical arsenic concentrations in the region are ranging from 500  $\mu$   $L^{-1}$  to 950  $\mu$   $L^{-1}$ . In particular, the knowledge of adsorption capacity of GEH may be employed as a design parameter for the construction of filters capable to remove arsenic from irrigation water used in the zone of Bajio.

### 2. Materials and methods

#### 2.1. Adsorbent

GFH (GEH), supplied by Wasserchemie (Germany), was the adsorbent used in this study. The particle size of the adsorbent used in this research fluctuated between 0.5 and 1.0 mm. This adsorbent has a large specific surface area and high porosity. The characteristics and properties of GEH reported in the literature are shown in Table 1.

# 2.2. Reagents

The surface morphology of GEH was determined by SEM; the images captured are shown in Fig. 1. The particle size has a regular distribution and the fine particles where removed by a previous washing with distilled water.

The GEH characterisation indicates that it is an amorphous material, without crystalline structure with more than two  $H_2$  atoms for each atom of Fe. The percentage of dry solids where of 55% with a particle size ranging from 0.5 to 1.0 mm.

Arsenate solutions were prepared by dissolving reagent-grade Na<sub>2</sub> HAsO<sub>4</sub>·7H<sub>2</sub> O provided by Sigma-Aldrich in distilled water. All of the chemicals used were of laboratory reagent grade (99.98% purity).

To study the impact of humic substances on the removal of arsenic, peat humic substances were employed (humic acid sodium salt from Sigma Aldrich). The extraction of fulvic acids from the humic substances was performed using the Shnitzer and Khan protocol (Chen et al. (1977)).

Stock solutions of HA and FA were prepared, and the total dissolved organic carbon (TOC) concentrations were determined using

**Table 1** Properties of GEH Amy et al. (2004).

Bulk density	$1.22-1.29 (g mL^{-1}) wet$
Bulk density	72-77%
Surface area	$250-300  (m^2  g^{-1})$
Moisture content	43-48%
Chemistry composition	$\beta$ -FeOOH and Fe(OH) <sub>3</sub>
pH <sub>ZPC</sub>	7.6-7.8
Grain size	0.32-2 (mm)

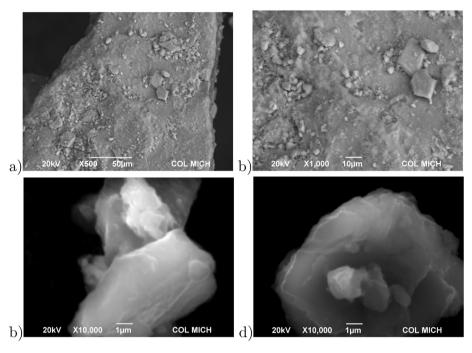


Fig. 1. SEM images for the GEH at a)  $500\times$ , b)  $1000\times$ , c)  $10\ 000\times$  and d)  $10\ 000\times$ .

a Shimadzu TOC-analyzer. Each sample was analyzed in triplicate, and in addition, various blanks were also analyzed for contamination control.

#### 2.3. Adsorption isotherms of arsenic (V)

An adsorption isotherm is used to evaluate the adsorption capacity and investigate the adsorption characteristics of a substance. An isotherm for HA was constructed using a quantity of GFH between 0 and 0.300 g in 500 mL flasks containing 0.800 mg  $L^{-1}$ arsenic (V) in solution and a TOC concentration of 6.5 mg  $L^{-1}$  HA. Using the same GFH quantities and arsenic (V) concentration, an isotherm for a TOC concentration of 6.5 mg  $\rm L^{-1}$  FA was constructed. The arsenic measurement was done in triplicate with a standard variation of 5, 7 and 3  $\mu$ g L<sup>-1</sup> for the WHS, HA and FA treatments respectively. The pH was adjusted to 7.4 for both isotherms so as to correspond with the average pH value found in a zone in Guanajuato, Mexico. The flasks were stirred at 220 rpm using a New Brunswick Scientific shaker for 24 h at 25 °C. In addition, an adsorption isotherm was made without humic substances (WHS). The pH of each sample was adjusted using a stock solution of either HNO<sub>3</sub> or NaOH. The pH was monitored thorough all the experiment and was keeping constant at 7.4  $\pm$  0.2. The volume of the bulk sample was modified by approximately 0.75% by adding stock solutions. The samples were collected after 24 h, filtered with a 0.45 µm cellulose nitrate filter and analyzed for arsenic by the molybdenum blue method. The molybdenum method has been used to determine low As(V) concentration in water (Lenoble et al. (2003)) and it has also been modified for faster and more accurate measurements of arsenate and phosphate in aqueous solutions (Tsang et al. (2007)).

# 3. Results

# 3.1. Adsorption isotherm

The Freundlich model is commonly used to estimate the

maximum adsorption capacity of arsenic (V). The mathematical expression of the Freundlich isotherm is given by Eq. (1);

$$q_e = K_F C_e^{1/n} \tag{1}$$

where  $C_e$  (mg L<sup>-1</sup>) is the pseudo-equilibrium concentration,  $q_e$  (mg g<sup>-1</sup>) is the amount of adsorbed arsenic at pseudo-equilibrium,  $K_F$  is a measure of the adsorption capacity at a specific solution phase concentration and 1/n is considered a measure of the surface heterogeneity and surface affinity for the solute.

Conversely, the Langmuir isotherm implies that the adsorption occurs on one superficial layer and that the adsorption rate balances the desorption rate, which is assumed as a constant adsorption energy and hence a uniform surface. The Langmuir model can be described by Eq. (2);

$$q = \frac{q_L b C_e}{1 + b C_e} \tag{2}$$

where q is the adsorption capacity,  $C_e$  is the adsorbate concentration at equilibrium,  $q_L$  is the maximum adsorption and b is the Langmuir constant related to the standard Gibbs free energy changes ( $\Delta G^0$ ).

Neither the Freundlich nor the Langmuir isotherm gives any information related to the adsorption mechanism. The DubininRadushkevich (D-R) isotherm model provides that information, as it distinguishes between ionic exchange adsorption and physical adsorption. To obtain an idea of the type of adsorption mechanism occurring, this isotherm was applied to the experimental data. The D-R isotherm is described by Eq. (3);

$$Q = q_{DR} \exp \left[ -k_{DR} \left( RT \ln \left( 1 + \frac{1}{C_e} \right) \right)^2 \right]$$
 (3)

where  $q_{DR}$  is the theoretical saturation capacity in mg g<sup>-1</sup>,  $k_{DR}$  is a constant that is related to the mean free energy of adsorption per mole of the adsorbate (mol<sup>2</sup> kJ<sup>-2</sup>), R is the ideal gas constant

(J mol<sup>-1</sup> K<sup>-1</sup>), and T is the absolute temperature (K). The constant  $k_{DR}$  is related to the free energy of adsorption per mole of the adsorbate (E, kJ mol<sup>-1</sup>). The value of E can be evaluated using the relationship given in Eq. (4) (Dubey and Gupta (2005));

$$E = \frac{1}{\sqrt{2k_{DR}}}\tag{4}$$

The value of E gives some information about the type of adsorption. If the free energy ranges from 8 to 16 kJ mol<sup>-1</sup>, the adsorption type is ion exchange, and if it is lower than 8 kJ mol<sup>-1</sup>, then the adsorption is due to physical adsorption (Mahramanlioglu et al. (2002)).

The experimental data obtained has been evaluated through the Pearson coefficient  $r^2$  and the standard error SE defined as,

$$SE = \sqrt{\frac{\sum_{i=1}^{N} q_i - q_i'}{N - 2}} \tag{5}$$

where q stands for the measured concentration and  $q_i'$  stands for the predicted value of the model.

The standard error provides us a measure of the relationship between the dispersion of individual observation with respect to the measured value. For the Freundlich model it is observed that the bigger standard error was obtained in absence of humic substances. The same behavior is observed the WHS treatment in the Langmuir model which has the greatest SE error. This implies that the variation of the measured value with respect to the predicted by the model is significant to describe accurately the experiments. However, as the humic substances are added the SE error diminishes, suggesting a good fit for all the models. For the DR model, the standard error was lower than 0.08 for all the treatments suggesting a good fit with respect to the experiments for all the treatments.

The goodness of fit was evaluated through standardized residuals defined as the ratio of the residuals over the estimated

variance and the lack of fit test. In Fig. 2 it is shown the standardized residuals for the regression model used in the isotherms. As observed, standardized residuals ranges from -2 to 2 and are randomly distributed around the x axis. This suggests that predicted values were closed to measured values with no over or under estimation of overall prediction and there is no pattern suggesting an error due to the chosen models. Thus, we conclude that our model fits reasonably well to the observed values.

As observed in Table 2, the lack of fit is significant for the three tested regression models. However, this fact does not invalidate the model since both the correlation coefficient  $r^2$  as well as the residuals are relatively small. In consequence, the large value of the lack of fit with respect to the pure error is due to a high precision of the experiments.

The parameters of the adsorption isotherms for arsenic (V) at 25 °C and a pH of 7.4 are shown in Table 3. The  $r^2$  of the Freundlich model was greater than 0.92, the  $r^2$  of the Langmuir model was greater than 0.87, and the  $r^2$  of the D-R model was greater than 0.90. The Freundlich model fits better for the WHS and FA cases than Langmuir and D-R models, while for the HA case, the Langmuir and D-R models fit better than the Freundlich model.

Table 3 shows that for all of the models, the adsorption capacity diminishes when humic substances are added; however the effect of adding FA instead of HA produces a lower adsorption capacity. The  $K_F$  values predicted by the Freundlich model for WHS, FA and HA were 2.589, 1.583 and 1.801 mg g<sup>-1</sup>, respectively, while the Langmuir model predicted adsorption capacities of 2.316, 1.709 and 1.766 mg g<sup>-1</sup> for WHS, FA and HA, respectively. Fig. 3 clearly shows the influence of humic substances on the adsorption isotherms of arsenic (V) for the Freundlich and Langmuir models at a pH of 7.4.

The D-R model presents adsorption capacities of 2.304, 1.544 and 1.748 mg g<sup>-1</sup> for WHS, FA and HA, respectively. The energy of adsorption (E) is defined as the free energy change when 1 mol of the ion is transferred from infinity in the solution to the surface of the solid. The E values were calculated by Eq. (4). Table 3 shows E

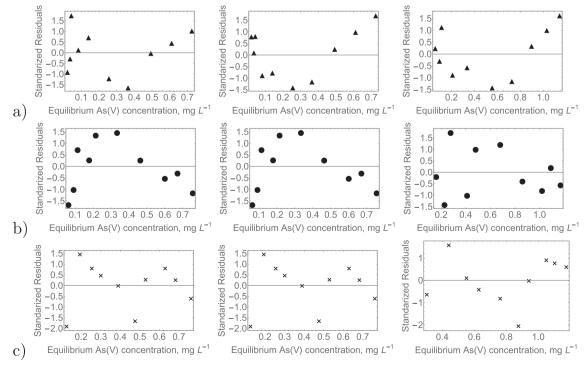


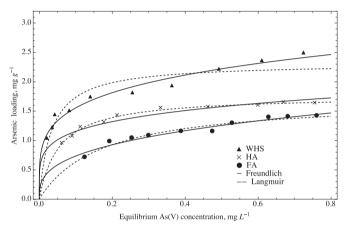
Fig. 2. Standarized residuals for a) Freundlich isotherm, b) Langmuir and c) D-R model, where 🛆 stands for WOM, • stands for AF and × stands for AH.

**Table 2** Error analysis for the isotherms.

	Freundlich			Langmuir			WHS	НА	FA
	WHS	НА	FA	WHS	HA	FA			
Pure Error	0.00473	0.01116	0.00192	0.00426	0.00680	0.00162	0.00061	0.00054	0.00001
Regression error Lack of fit	0.01645 0.01172	0.03836 0.02719	0.00923 0.00731	0.02875 0.02449	0.04636 0.03955	0.00892 0.00730	0.02065 0.01453	0.00030 0.00024	0 .00008 0.00007

**Table 3**Freundlich, Langmuir and Dubinin-Radushkevich parameters for arsenic (V) test at pH 7.4 in presence of FA, HA and WHS.

Isotherm Models												
Humic substances Freundlich		Langmuir			Dubinin-Radushkevich			Е	$r^2$	SE		
	$K_F$	N	r <sup>2</sup>	SE	$q_L \ { m mg g^{-1}}$	b	r <sup>2</sup>	SE	$q_{DR} \  m mg \ g^{-1}$	kJ mol		
WHS	2.589	0.221	0.967	0.093	2.316	29.940	0.874	0.183	2.309	7.480	0.905	0.079
FA HA	1.583 1.801	0.333 0.193	0.952 0.928	0.052 0.070	1.709 1.766	5.930 18.516	0.951 0.987	0.052 0.029	1.544 1.748	4.429 6.421	0.946 0.986	0.047 0.023



**Fig. 3.** Adsorption isotherms of arsenic (V) obtained by using Freundlich and Langmuir model in presence of FA, HA and WHS.

values of 7.480, 4.429 and 6.421 kJ mol<sup>-1</sup> for WHS, FA and HA, respectively, and these values suggest that adsorption mechanism is physical in nature (weak van der Waals forces) because these values are lower than the limits mentioned above. Fig. 4 shows the experimental data and the fitted model using the D-R isotherm

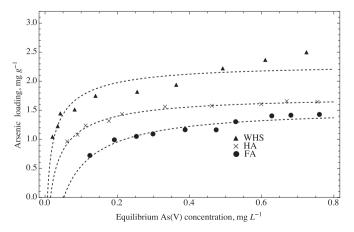


Fig. 4. Adsorption isotherms of arsenic (V) obtained by using the D. R. model in presence of FA, HA and WHS.

equation for WHS, FA and HA.

Using the Langmuir parameters, it is possible to calculate the standard Gibbs free energy change using Eq. (6);

$$\ln\left(\frac{1}{b}\right) = \frac{\Delta G^0}{RT} \tag{6}$$

where b is the Langmuir constant shown in Table 3, R is the universal gas constant (J mol<sup>-1</sup> K<sup>-1</sup>) and T is the absolute temperature (K). The results obtained for WHS, FA and HA were -8.421, -4.410 and -7.231 kJ mol<sup>-1</sup>. The negative values of  $\Delta G^0$  indicate that the adsorption proceeds spontaneously.

# 3.2. Removal kinetics

The removal kinetics of arsenic (V) in the presence of FA, HA and WHS are shown in Fig. 5. The results indicate a rapid initial uptake rate of arsenic (V) followed by a slower removal rate, which finally approaches a plateau. The results show that humic substances diminish the rate constant. The presence of humic substances affects the behavior of the removal kinetics, which are controlled by the accessibility and availability of the surface sites, the relative surface charges, the adsorbed species, and the complexation rate of the dissolved species with the surface sites (Smith (1998)). The removal efficiency values, defined as the ratio of the equilibrium

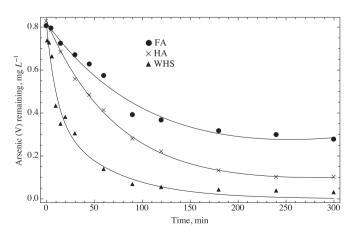


Fig. 5. Adsorption kinetics of arsenic (V) in presence of FA, HA and WHS.

arsenic concentration to the initial arsenic concentration, were calculated. The removal efficiency of arsenic (V) ranged from 69 to 71% and from 93 to 95% in the presence of FA and HA, respectively, while the removal efficiency raged from 98 to 99% WHS.

To evaluate the order of the kinetics, first order and second order models were applied. The kinetic models were tested by least-square regression analysis to determine which equation best described the data set. The correlation coefficient  $(r^2)$  and the standard error (SE) were calculated for each kinetic model. The values of  $r^2$  and SE for the tested kinetic models are shown in Table 4. The SE values for the second order kinetic model are lower than those for the first order kinetic model; this suggests that the second order kinetic model generally describes the experimental data better in all cases.

Table 5 shows the second order rate constants (k) in the presence of FA, HA and WHS. The correlation coefficients  $(r^2)$  ranged from 0.951 to 0.977, while the values of k ranged from 0.009 to 0.116 L mg<sup>-1</sup> min<sup>-1</sup>.

The lowest rate constant occurred in the presence of FA. The presence of HA affects the rate constant in a similar way. Consequently, the smaller equilibrium constant probably comes from occupation and obstruction of the adsorption sites by the organic matter, thereby decreasing the removal rate.

As can be observed, the first order kinetic model has a lower  $r^2$  value than the second order kinetic model. Thus, the goodness of fit will be only checked for the second order kinetic model. In Fig. 6 the standardized residuals for the second order kinetic model are shown. It can be observed that the residuals are distributed randomly around the x axis, besides all the residuals are distributed inside the region of 1.5 around the x axis. This results indicates that the regression analysis describes the model reasonable well.

The influence of fulvic and humic acids on the removal of arsenic by kaolinite was studied by Saada et al. (2003). These authors suggest that arsenic adsorption occurs first on humic acid sites and then, once they were saturated, on the remaining kaolinite sites leading to better arsenic removal in the presence of humic acids than in the presence of fulvic acids (with a ratio of the concentrations of humic acids:arsenic on the order of 10<sup>4</sup>). Conversely, Pallier et al. (2010) found that arsenic removal by kaolinite was not affected by the presence of fulvic acids under a ratio of the concentrations of humic acids:arsenic on the order of 10<sup>2</sup>. However, in the present study, it was found that even at a ratio of the concentrations of humic acids:arsenic on the order of 10. there was a clear

**Table 4** Pearson coefficient  $(r^2)$  and standard error (SE) for the kinetic models tested.

Kinetic Models				
Humic Substances	First order $\ln \frac{[As_t]}{[As_0]}$ vs $t$		Second $\frac{1}{[As_0]} - \frac{1}{[As_0]}$	vs t
	SE	r <sup>2</sup>	SE	r <sup>2</sup>
WHS	0.167	0.838	0.065	0.977
FA	0.070	0.879	0.041	0.951
HA	0.059	0.937	0.053	0.972

**Table 5**Rate constants in presence of FA, HA and WHS

Humic Substances	$K$ mg $^{-1}$ L min $^{-1}$	r <sup>2</sup>
WHS	0.116	0.977
FA	0.0092	0.931
НА	0.0313	0.972

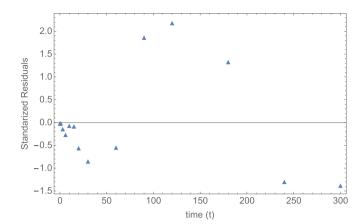


Fig. 6. Standarized residuals for the second order kinetic model.

impact on the removal of arsenic by GFH in the presence of humic acids.

The influence of organic matter on the removal of arsenic by hematite has been studied by Redman et al. (2002). These authors suggest that the complexation of organic matter and arsenic is strong enough to enhance the mobility of arsenic if the organic matter is introduced into the system with the arsenic.

Ko et al. (2007) studied the effect of the removal of inorganic arsenic species by hematite in the presence of humic acids. These authors suggest that the presence of humic acids leads to a decrease in the arsenic adsorption, which is compatible with the results presented in this study.

#### 4. Conclusions

The results presented in this work emphasize the importance of humic substances on the removal of arsenic (V) by GFH. This study evaluated the effect of humic substances on the adsorption of arsenic (V) onto GFH. The results indicated that HA and FA could enhance the mobilization of arsenic (V) under the conditions employed, thereby reducing its removal efficiency. This mobilization could be related to the complexation between the arsenic and humic substances, which therefore avoids the adsorption of arsenic (V) onto GFH.

The equilibrium data fit well into the Langmuir, Freundlich, and Dubinin-Radushkevich isotherms. These isotherm models describe the adsorption of arsenic (V) reasonably well. The adsorption capacity for all of the models decreases when humic substances are added. In particular, the adsorption capacity with FA was lower than with HA. Information from  $\Delta G^0$  showed that the adsorption process was spontaneous, and information about E suggested that the adsorption is physical in nature due to the low value of E ( $\leq 8$  kJ mol $^{-1}$ ).

The kinetic equilibrium of removal was reached in the first 150 min, and approximately 74% and 94% of the arsenic (V) was removed in this period with FA and HA, respectively. The measured kinetic data for the removal of arsenic (V) fit well to a second-order kinetic model.

However, further studies are required to understand (i) the nature and type of bonds between arsenic and humic substances and the stability of these bonds and (ii) the role of humic substances and their bonds in the adsorption process and elucidate the difference between the bonds that can occur between the FA and HA separately in the GEH.

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