



Experimental and Kinetic modeling of As (V) adsorption on Granular Ferric Hydroxide and Laterite

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Abstract

This work aims to study the As (V) removal in aqueous solutions using Granular Ferric Hydroxide (GFH) and Natural Laterite at ambient temperature. Column experiments were conducted to investigate the As (V) removal mechanism and effects of parameters affecting the adsorption were studied to follow the adsorption kinetics. Maximum removal of arsenic (99.99% and 99.5%) was achieved at 15 min of contact time with an initial concentration of 20 mg/L using 10 g of GFH and laterite in 50 ml volume of solution, respectively. From the isotherm models study, i.e. Langmuir, Freundlich and Dubinin - Radushkevich, the adsorption process in our study followed best Freundlich isotherm. The study of isotherms showed that the adsorption was physical, spontaneous with GFH while endothermic using laterite, respectively. The kinetics study showed that the adsorption process fits with a pseudo-second order reaction model using both adsorbents. The adsorption column design was done using Logit method and the obtained values of adsorption rate coefficient (K) and adsorption capacity coefficient (N) were 3.2 10⁻⁴ L/(mg. min) and 8968.46 mg/L, respectively for GFH and 1.43 10⁻³ L/(mg. min), 977.19 mg/L using laterite. The fixed bed column studies showed that Granular Ferric Hydroxide and Laterite were efficient in small-scale for As (V) removal.

Keywords: Arsenic, Removal, Granular Ferric Hydroxide, Laterite, aqueous solutions.

1-Introduction

Arsenic contamination of surface and subsurface waters is reported in many parts of the world and is considered a global issue. As a naturally occurring toxic substance in the earth's crust, arsenic enters into aquifers and wells through natural processes, and to the water cycle as a result of anthropogenic activities [1]. Arsenic pollution has been reported in countries such as Bangladesh, USA, west Bengal, Mexico, Chile, Taiwan and many others [2]. Vietnam and Burkina Faso are among these countries requiring the research studies.

It's well known that the ingestion of inorganic arsenic can result in both cancers (skin, lung, liver and urinary bladder) and non-cancer effects such as melanosis, hyperkeratosis, and prostate [3]. Population-based studies showed that arsenite [As (III)] and arsenate [As (V)] that are inorganic and more toxic forms may adversely affect several organs in the human body [4]. In Northern of Burkina Faso, Yatenga Province is known for polluted groundwater by arsenic. Arsenic pollution in this area was due to arsenopyrite specie in bedrock [5]. SOME *et al.* [5] showed that the arsenic concentration in water from tube

wells was ranging between 1 and 124 µg/L while 87% of villagers use the water from tube wells. Among the first recognized consequences from chronic exposure to arsenic was melanosis, a skin disorder of hyperpigmentation or keratosis where the skin goes rough and dry with skin papules [5]. A study in Vietnam on Red Delta River showed that 48% of ground waters in rural Hanoi area have arsenic concentrations exceeded Vietnam guideline on arsenic in drinking water [6].

Some treatment technologies have been developed to remove arsenic from drinking water and groundwater under both laboratory and pilot-scale conditions including coagulation, advanced oxidation processes, ion exchange and adsorption [7]. However, their implementation inquires the use of adsorbent such as silicate, clay, ferric hydroxide, maize cob, rice husk, Activated Carbon and other composite materials [8]. In addition of these adsorbents, laterite and Granular Ferric Hydroxide have been used in previous studies by many authors given their particularities [9, 10]. In Burkina Faso, Granular Ferric Hydroxide has been tested successfully at laboratory column scale and found efficient for the arsenic removal [11]. Natural Laterite from Burkina Faso showed a low arsenic removal capacity in column experiments [12]. However, Laterite from Vietnam was tested and found efficient with an arsenic removal capacity of 600 µg/g and 1100 µg/g for As (III) and As (V), respectively [13].

The objective of this present study was to assess the potential and applicability of Granular Ferric Hydroxide

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(GFH) and Natural Laterite for removing As (V) in aqueous solutions.

Langmuir, Freundlich, Dubinin – Radushkevich equations were used to fit the isotherm models. Pseudo-first and pseudo-second order kinetic models were applied to evaluate the mechanism of As (V) adsorption. Logit method was employed to design the behavior of column adsorption.

2- Materials and Methods

2.1 Samples preparation

As (V) solutions were prepared by diluting in doubly distilled water a standard solution of arsenical acid (H_3AsO_4) of 1000 mg/L concentration obtained commercially to get 20 mg/L concentrations which were used during the experiments.

2.2 Adsorbents preparation

Granular ferric hydroxide (GFH) was obtained from the manufacturer Wasserchemie GmbH (GEH), Germany. The material is predominantly Akaganeite, a specific form of an iron oxide mineral [14]. The characteristics of GFH reported in the literature [14] are summarized in Table 1.

Table 1: Characteristics of GFH [14].

Properties	Quantitative value
pH_{ZPC}	7.6 – 7.8
BET Surface (m^2/g)	240 - 300
Bulk density (g/mL)	1.19
Grain size (mm)	0.32- 2
Porosity (%)	72 – 77
Moisture content (%)	43 - 48

Natural Laterite used in this work was reddish brown color and collected from Lâm Đông Province at 300 Km of Ho Chi Minh City (Vietnam). Before its use as adsorbent, the collected samples were prepared as shown on figure 1 to obtain the similar GFH grain size:

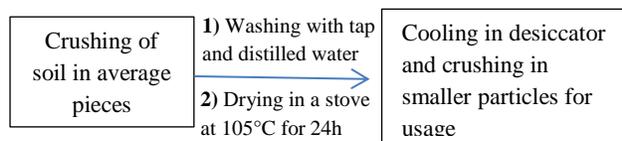


Figure 1: Different steps of Laterite preparation

2.3 Laterite characterization

Elemental composition of laterite was done by Energy Dispersive Spectroscopy (EDS) and Scanning Electron Microscopy (SEM) was used to determine the surface morphology of the material. The pH at Zero Point Charge (pH_{ZPC}) was determined according to the method described by NOH *et al.* [15] and bulk density evaluated using the method described by LASKA [16].

Brunauer – Emmett - Teller (B.E.T) experiments were used for the surface area determination and the dimensional analysis was employed to determine the volume and radius of pore using Quantachrome NovaWin - NOVA instruments. A Fourier Transform-Infrared spectrum of laterite material was recorded to study the surface

functional groups using an infrared spectrophotometer (TENSOR 27 - BRUKER - GERMANY) in the range of 400 - 4000 cm^{-1} .

2.4 Arsenic removal experiments and analysis

Continuous fixed bed adsorption was carried out with ion exchange column (internal diameter 2.8 cm, length 22.5 cm). Natural Laterite of 0.45–2.5 mm particles size was used as adsorbent in the experiments.

In order to remove the red color of material, the system was filled and washed with distilled water 5 times. Influent water was filled in the column manually and effluent water was collected by gravimetry (Fig.2). Arsenic content in water was analyzed by Hydride Generation - Atomic Absorption Spectrophotometer (HG - AAS) with mercury hydride system at a wavelength of 193.7 nm using electrode discharge lamp (EDL). The instrument was calibrated with arsenic standard solutions of concentrations ranging from 1 to 20 $\mu g/L$. The detection limit of Arsenic was of 1 $\mu g/L$.

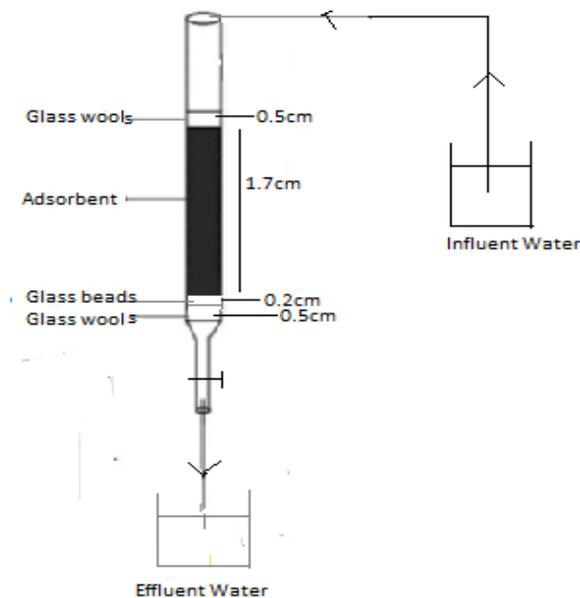


Figure 2: Experimental device of column setup

Arsenic removal percentage was calculated as follows:

$$\% \text{ As Removal} = \frac{C_0 - C_e}{C_0} * 100 \quad (1)$$

where C_0 and C_e are the concentration of arsenic in influent and effluent water ($\mu g/L$), respectively.

3 Results and Discussion

3.1 Characterization of laterite

Elemental composition of laterite and its physical-chemical characteristics are provided in table 2. Data reported in this table showed that laterite contains mostly Si, Al, Fe and pH_{ZPC} is slightly basic. The dimensional analysis showed that laterite particles were microporous. The lateritic soil has pH_{ZPC} , porosity and bulk density

higher than those of GFH and a small surface area compared to GFH as shown by BET experiments.

Table 2: Characteristics and composition of laterite

Properties	Quantitative value
pH _{ZPC}	7.97
BET surface (m ² /g)	10.96
Micropore volume (cm ³ /g)	0.01
Pore radius (nm)	1.16
Grain size (mm)	
Bulk density (g/mL)	0.45- 2
Moisture content (%)	1.91
Residual porosity (%)	0.43
	97- 99
Elemental composition (% , wt/wt)	
Si	34.27
Al	19.86
Fe	7.79
Mg	5.06
Ca	4.59
Ti	1.68
Na	1.31
C	4.4
O	19.87

Scanning electron microscope image at 55 magnifications of laterite particles is presented in Fig. 3 and Energy dispersive spectroscopy spectrum in Fig. 4.

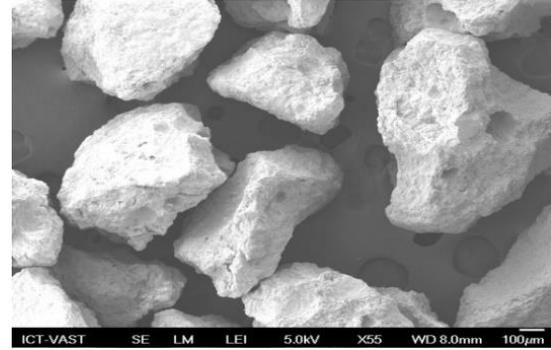


Figure 3: SEM image at X55 of laterite particles

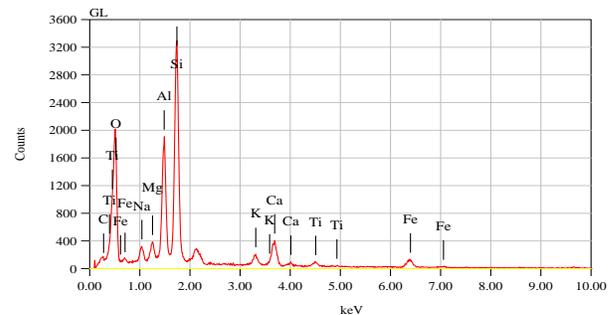


Figure 4: Energy dispersive spectroscopy spectrum of laterite.

FT-IR spectrum of laterite is shown in Figure 5. The adsorption band around 3435 cm⁻¹ (Fig.5) is attributed to the OH group of Fe, Al and Si minerals [17, 18]. The band at 1639 cm⁻¹ is assigned to interlayer water molecules [17, 18]. The band around 789 cm⁻¹ can be attributed to the Al-O bond stretching. Others surface hydroxyl groups stretching's by bands at 3692 and 3623 cm⁻¹ are observed. The band at 1036 cm⁻¹ corresponds to the Si-O bond. The Fe-O bond stretching was observed at 542 cm⁻¹ and bands at 469, 429cm⁻¹ suggest a possible presence of Si-O-Si bonds [18].

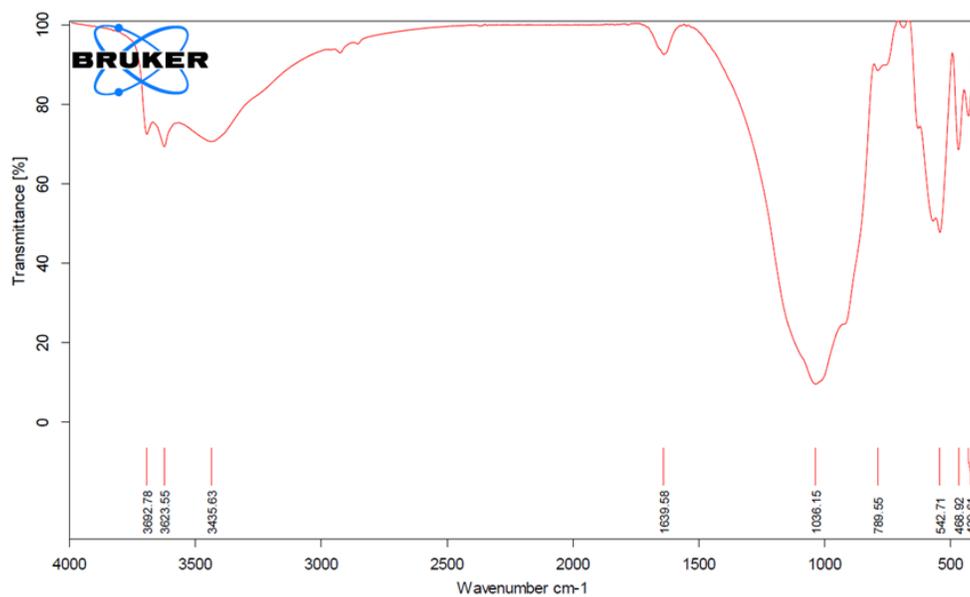


Figure 5: FT-Infrared spectrum of laterite

3.2 Fixed bed column experiments

3.2.1 Effect of flow rate

The effect of flow rate on As (V) adsorption was studied by varying the flow rate from 3.3 to 40 mL/min. Arsenic (V) removal percentage decreases from 99.99 to 98.3% using GFH and from 99.5 to 97% using laterite when the flow rate increases (figure 6). This phenomenon can be explained by insufficient residence time of the solute in the column [19]. Indeed, an increase of flow rate causes a decrease of the residence time which lowers the removal efficiency [20]. As (V) retention by GFH higher compared to laterite as shows on figure 6 as a result of large surface area and low porosity of GFH than laterite used in this study.

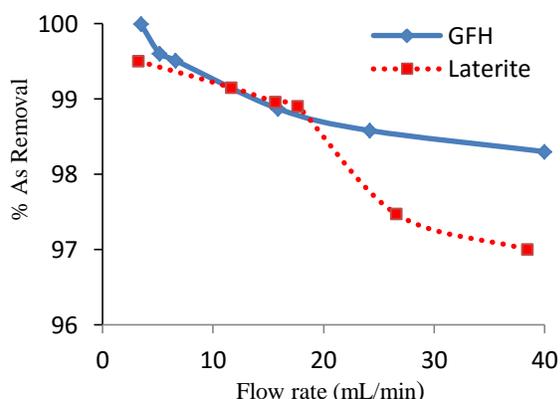


Figure 6: Effect of flow rate on arsenic removal using 10 g of adsorbent and $C_0=20$ mg/L.

3.2.2 Effect of contact time

The effect of contact time on the adsorption of As (V) on GFH and laterite adsorbents was studied within the range 5 - 60 min (figure 7). The removal of arsenate ions as a function of time suggested a slight change of the removal percentage from 5 to 45 min. Thereafter, no change in adsorption was found. Trend of initial uptake increase is low as a consequence of the availability of initial active binding sites on the adsorbent surface [21]. According to this data, material surface saturation was reached after 45 min of contact time with GFH and around of 30 min using laterite. This difference could be attributed to the higher porosity of laterite.

3.2.4 Effect of initial pH

The initial pH value is an important parameter of column adsorption studies. pH of samples was ranged from 3 to 11. Optimum removals of 99.89% and 98.5% were obtained using GFH and laterite, respectively (figure 8). Arsenic removal increased with pH from 99.67 to 99.89% using GFH but decreases from 98.5 to 97.5% when pH increased between 3 and 9 with laterite. No variation in arsenic removal was observed between pH 9 and 11. The increase observed in arsenic removal between pH 3 and 9 could be explained to the significant quantity of hydronium

ions and positive charges on laterite surface which favorite the adsorption of arsenate ions until pH 9.

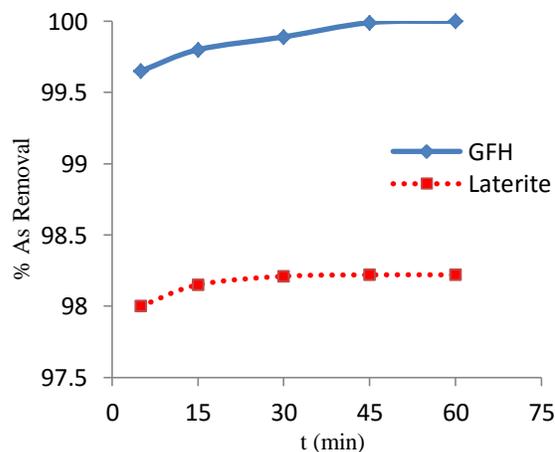
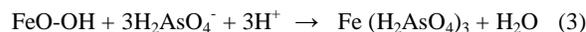


Figure 7: Effect of contact time on arsenic removal using 10 g of adsorbent and $C_0=20$ mg/L.

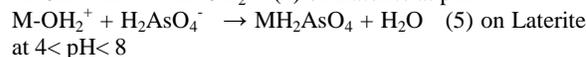
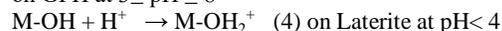
After pH 9, the constant part is the result of repulsion with hydroxyl ions involving an ion exchange represented by the following equation [10, 22]:



Change in arsenic removal rate can be also attributed to the complexation reactions on the adsorbent surface being highly favored at different values of pH [23, 18]. The following reactions mechanisms can be produced:



on GFH at $3 \leq \text{pH} \leq 8$



M= Fe, Al or Si

3.2.5 Effect of initial concentration of As (V)

The adsorption behavior of As (V) was studied with arsenic initial concentrations ranging from 5 to 40 mg/L. The removal of As (V) on laterite adsorbent increased from 92.9 to 99% when the initial arsenic concentration increased with maximum removal rate of 99.11% (figure 9). This increase could be the result of the occupation of free sites, inaccessible at low concentrations of adsorbate [24]. However, no significant change in arsenic removal was observed using GFH (fig. 9).

3.2.6 Fixed bed column design

The fixed bed column was designed by Logit method described by the following equation [26]:

$$\ln\left(\frac{C}{C_0-C}\right) = KC_0 \cdot t - \frac{KN}{v}x \quad (6)$$

where C is the arsenic concentration at any time t , C_0 initial arsenic concentration, v the approach velocity (cm/min), x the bed depth (cm), K the adsorption rate constant (L/mg).

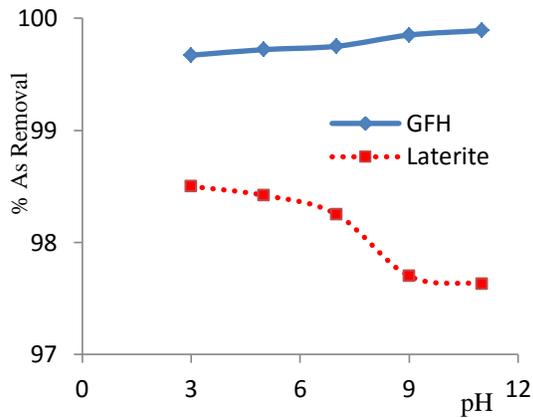


Figure 8: Effect of initial pH on arsenic removal using 10g of adsorbent for 15 min with $C_0=20$ mg/L.

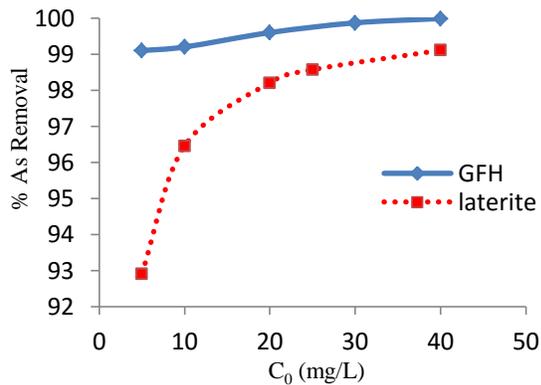


Figure 9: Effect of initial concentration on arsenic removal using 10 g of adsorbent for 15 min.

min), and N is the adsorption capacity coefficient (mg/L). Plot of $\ln[C/(C_0-C)]$ versus t (Fig. 10) gives a straight line with slope $K C_0$ and intercept $K.N \frac{x}{v}$ from which K and N could be calculated.

Adsorption rate coefficient (K) and adsorption capacity coefficient (N) were $3.2 \cdot 10^{-4}$ L/(mg. min) and 8968.46 mg/L using GFH, and $1.43 \cdot 10^{-3}$ L/(mg. min) and 977.19 mg/L with Laterite, respectively. The values allow knowing the column capacity and material efficiency which shows a higher adsorption capacity of GFH compared to Laterite.

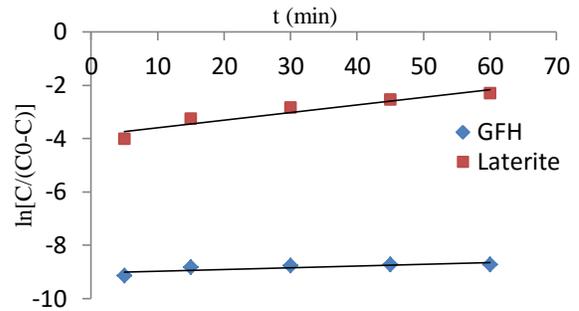


Figure 10: Linearized form of Logit model.

3.3 Adsorption isotherms study

The distribution of the adsorbate between the surface of adsorbent and the solution at given temperature has been described by Langmuir and Freundlich isotherms. The following equations were used to follow the isotherm models [27-29].

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{b Q_m} \quad (7)$$

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (8)$$

In addition to these isotherms widely used, D-R isotherm can be used to describe the free energy of adsorption. The obtained data from fixed bed column experiments were applied to linearized forms of these models.

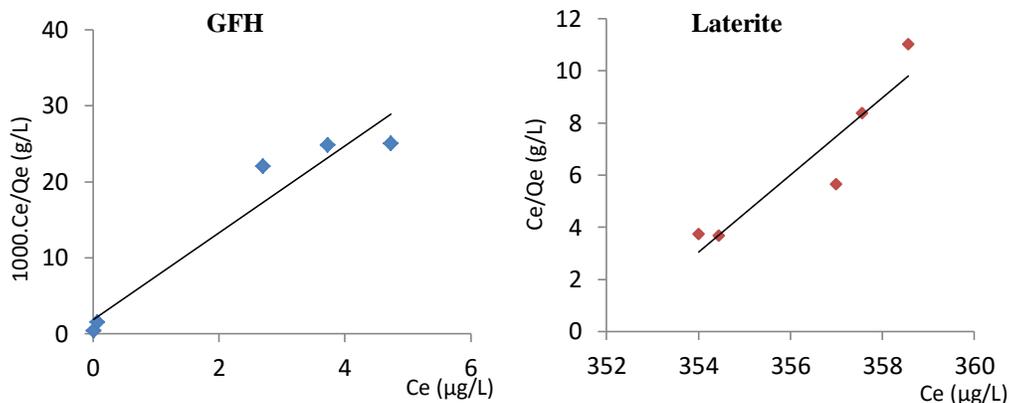


Figure 11: Langmuir's plots for kinetic modeling of As (V) adsorption by GFH and Laterite with $m =10$ g for 15 min and $C_0= 20$ mg/L.

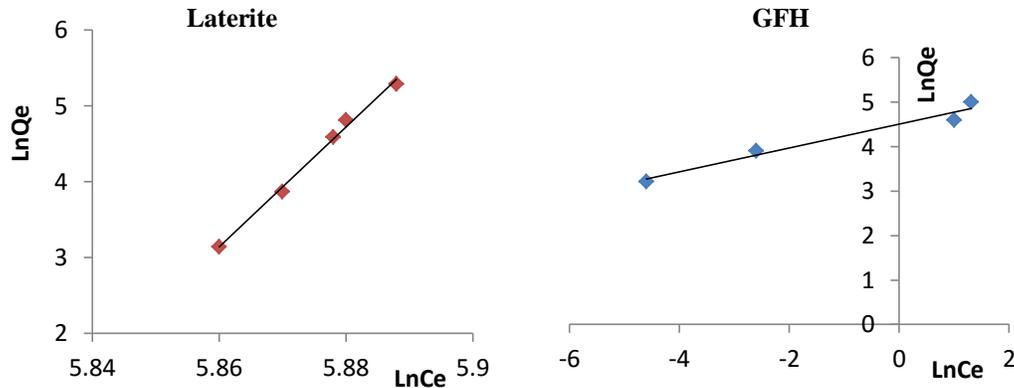


Figure 12: Freundlich's plots for kinetic modeling of As (V) adsorption by GFH and laterite with m=10 g for 15 min, C₀= 20 mg/L.

Table 3: Constants of Langmuir and Freundlich.

Adsorbent	Langmuir constants			Freundlich constants		
	Q _m (μg/g)	b (L/μg)	R ²	n	K _F (μg/g)	R ²
GFH	0.17	3.035	0.93	3.72	91	0.96
Laterite	0.67	0.003	0.86	2	17.28	0.99

Data reported in table 3 showed that Langmuir isotherm is unfavorable while Freundlich isotherm is favorable for the adsorption process. Hence, the applicability of Freundlich isotherm allowed predicting that the adsorption is done on multilayer in the present studies. From Langmuir constant b, the free energy of Gibbs can be expressed by following relation [2]:

$$\Delta G^\circ = -RT \log b \quad (9)$$

The calculated values of free energy were -2.75 and 14.38 KJ/mol using GFH and laterite, respectively. This shows that the process is spontaneous and endothermic on GFH and laterite, respectively. The endothermic process is stable energetically on laterite [30, 31]. In order to predict the efficiency of the adsorption process and assess if the process is favorable or unfavorable, the dimensionless equilibrium parameter R_L was determined using the following equation [32]:

$$R_L = \frac{1}{1 + bc_0} \quad (10)$$

Values of R_L were found to be ranged from 0.84 10⁻⁵ to 6.510⁻⁵ and 0.82 10⁻² – 6.25 10⁻² using GFH and laterite, respectively showing that the adsorption process is favorable (R_L values between 0 and 1).

It is clearly known that the constants of Langmuir and Freundlich isotherms don't suggest anything about the adsorption mechanism. In order to understand the adsorption type and mechanism, the experimental data were used with Dubinin- Radushkevich isotherm model [33].

$$\ln Qe = \ln Q_m - K \cdot \epsilon^2 \quad (11)$$

Polanyi potential (ε) can be calculated by the following relation:

$$\epsilon = RT \cdot \ln \left(1 + \frac{1}{c_e} \right) \quad (12)$$

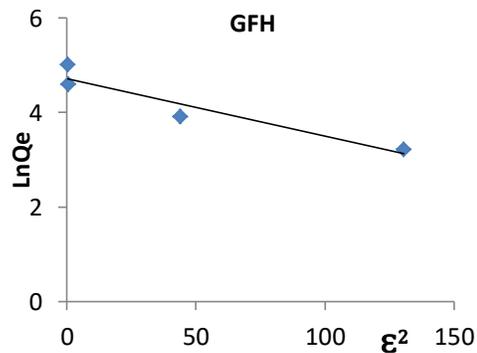


Figure 13: D-R plot for kinetic modeling of As (V) adsorption by GFH with m= 10 g for 15 min of contact.

The mean free energy of adsorption (E) defined as the free energy change when one mole of ion is transferred to solid surface from infinity in solution was calculated using [34]:

$$E = (2K)^{-0.5} \quad (13)$$

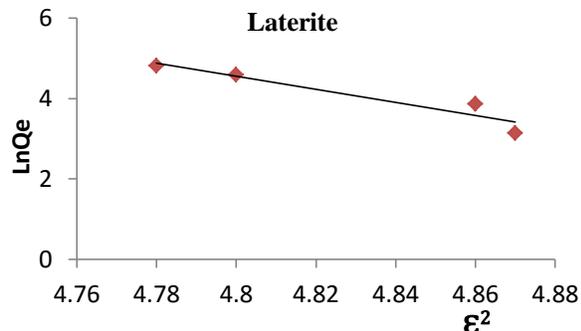


Figure 14: D-R's plot for kinetic modeling of As (V) adsorption by laterite with m =10 g for 15 min of contact.

Table 4: Constants of D-R isotherm

Adsorbent	Qm μg/g	K mol ² /KJ ²	R ²	E KJ/mol
GFH	112	0.012	0.90	6.4
Laterite	170	1.013	0.90	0.17

The found values of E were 6.4 and 0.17 KJ/mol less than 8 KJ/mol. This indicates that the adsorption is physical confirming a multilayer adsorption with Freundlich isotherm. This result is in agreement with previous works where it was concluded that the GFH surface is very heterogeneous [35]. We can conclude that the adsorption process is physical, reversible, produced on multilayer and engages the Van Der Waals and polarization forces using both materials (GFH and Laterite).

3.3 Adsorption kinetics

In order to investigate the mechanism of arsenic adsorption onto both materials, two kinetic models were used. The pseudo-first-order equation of Lagergren [36] based on the solid capacity and pseudo-second-order reaction model of Ho *et al.* [37] based on the solid phase sorption were analyzed. The following equations were used out to follow the adsorption kinetics [36, 37].

$$\ln(Qe - Qt) = -K_1t + \ln Qe \quad (14)$$

Table 5: Constants of pseudo-first and pseudo-second order reaction models.

Reaction order	Adsorbent	K	Qe cal (μg/g)	Qe exp (μg/g)	R ²
Pseudo-first model	GFH	0.081	0.015	100	0.95
	Laterite	0.001	1.87	98.2	0.96
Pseudo-second model	GFH	14.28	100	100	1
	Laterite	0.346	98.04	98.2	1

Higher values of correlation coefficient (R²) were found for the pseudo-second order model compared to pseudo-first order reaction model. In addition, the

$$\frac{t}{Qt} = \frac{1}{Qe} t + \frac{1}{K_2 Qe^2} \quad (15)$$

With Eq. (14) is for the pseudo-first order model and Eq. (15) for the pseudo-second order model. The application of these equations has given the following graphs.

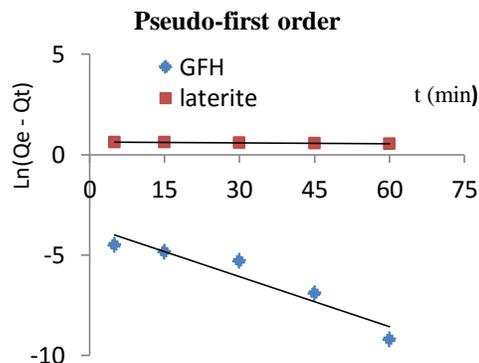


Figure 15: Lagergren's plot for pseudo-first order kinetics of As (V) adsorption by GFH and laterite with m =10 g, C₀= 20 mg/L.

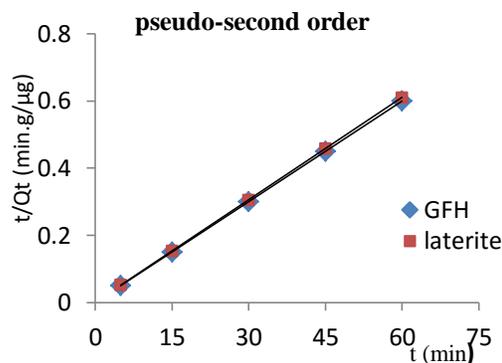


Figure 16: Ho and Mckay plot for pseudo-second order kinetics of As (V) adsorption by GFH and laterite with m =10 g, C₀= 20 mg/L.

calculated values of adsorption capacity Qcal were well comparable to experimental values Qexp (Table 5) using the pseudo-second-order model. These results indicated that

the kinetics of As (V) adsorption using both materials (GFH and Laterite) can be explained by pseudo-second order kinetic model. The constants of adsorption rate are 0.346 and 14.28 g/($\mu\text{g} \cdot \text{min}$) using Laterite and GFH, respectively.

4 Conclusion

In this present study, Laterite and GFH have been used as adsorbents in As (V) removal and found efficient using column operations. The adsorption process followed Freundlich and Dubinin – Radushkevich isotherm models. The free energy of adsorption E values allowed concluding that the adsorption is a physisorption using both adsorbents. From free energy of Gibbs, it is concluded that the adsorption process is exothermic and spontaneous using laterite and GFH, respectively. The values of dimensionless equilibrium parameter (R_L) showed that the adsorption is favorable using both adsorbents. The mechanism of the adsorption process follows the kinetics of the pseudo-second order reaction.

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