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Laterite, Sandstone and Shale as Adsorbents for the Removal of Arsenic from Water

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Abstract

This study aims at exploring arsenite (As (III)) removal from water using naturally available rocks (laterite, sandstone and shale) in Côte d'Ivoire. The study focused on the adsorbent dose, operating pH, contact time, initial arsenite concentration, and modelisation on the removal of arsenite by performing batch adsorption experiment with well water. The optimal dosage related to an initial As (III) concentration of 5 mg/L was about 50, 75 and 145 g/L for laterite, sandstone and shale respectively. Laterite has a better adsorption capacity in comparison to sandstone and shale. On the other hand, kinetic study reveals that the equilibrium times are 5 h for laterite, 3 h for sandstone and 8 h for shale. Results showed that laterite, sandstone and shale could remove the arsenic in groundwater at initial arsenic concentrations below 5 mg/L, satisfying the World Health Organization (WHO) standard for drinking water. Moreover, kinetics study showed that the overall adsorption rate of arsenite was described by the pseudo-second-order kinetic model.

Keywords

Adsorption, Arsenite Removal, Laterite, Sandstone, Shale

1. Introduction

Groundwater is the primary source of drinking water for many densely-populated countries in the world [1]. These dangerous arsenic concentrations in natural waters are now a worldwide problem and often referred to as a 20th - 21st century calamity. Indeed, according to WHO [2], arsenic contamination has

aroused attention due to groundwater levels in many parts of the world at much higher concentrations than the maximum contaminant level of 10 μg/L for arsenic in drinking water. Many problems of health from arsenic contained in drinking water have been observed in Bangladesh [3], in Vietnam [4] in Cambodia [5] and Burkina Faso [6]. In Akouédo (Côte d'Ivoire), high Arsenic concentrations in drinking water from well have been recorded in our previous work [7]. In fact, in this area, well water is the main source of drinking water supply. So, the presence of the arsenic in these underground waters will cause problems. Thus, several conventional processes for treatment of arsenic like coagulation-flocculation [8], co-precipitation [9], ion-exchange [10] and nanofiltration process [11] have been reported. However, these processes involve production of high arsenic contaminated sludge [12], high maintenance cost and require relatively expensive mineral materials [13]. Therefore, an effective arsenic removal technology is thus highly desirable to provide safe drinking water to the affected people. Adsorption is gaining importance in recent days due to its technical simplicity and easier applicability in developing countries. This research work aims at removing arsenic from aqueous solutions by the geo-materials like laterite, sandstone and shale. The specific objectives are 1) to determine optimal dose, the kinetic parameter of arsenic (III) adsorption, and 2) to study the effect of pH, time, and initial concentration on the arsenic (III) adsorption.

2. Materials and Methods

2.1. Adsorbate and Adsorbents

As (III) stock solution (1000 mg/L) was prepared by dissolving reagent grade As (III) oxid of 99.5% purified into deonized water. The volume of the solution was made up to 1L in a standard flask. The working solutions containing arsenic were prepared by dissolving appropriate amount of arsenic from stock solutions in well water. The pH of well water varied from 6.3 to 6.6. The experiments were performed at ambient temperatures up to 25˚C.

Laterite contained goethite, quartz, hematite, gibbsite and kaolinite, while sandstone main components were goethite, quartz and hematite. In this shale, appear mainly, small crystals of quartz, albite, microcline, chlorite, kaolinite and dolomite. The data of elemental composition of laterite highlights that silica represents 20% of the material, while the percentage of potential adsorbents mineral oxides Al_2O_3, Fe_2O, MgO and MnO was about a 63.13%. Concerning sandstone, it contained more silica (57.76%) than potentially adsorbent mineral (36.58%) [14]. In shale, the most abundant element here is silica (SiO_2 55.43%) followed by alumina (Al_2O_3 15.46%) and iron oxide Fe_2O_3 (9.21%). Other oxides (MnO, MgO, CaO, Na_2O; K_2O; TiO_2) in very small proportions, between 0.29% and 3.13%, are also contained in it. The rate of constituent elements potentially adsorbent minerals is 27.98%. This support contains oxide of calcium with a rate of 2.34% [15]. The CEC of laterite, sandstone and shale are respectively 34.1; 4.7

and 33.13 mEq/100g.

2.2. Batch Adsorption Experiments: Optimal Dose Measurement

Batch experiments were performed by adding the sorbent in bottles (500 mL) and aqueous As (III) solution at desired initial pH. For all experiments, initial pH of As (III) solution was controlled with a pH-meter by adding nitric acid (HNO₃) and/or sodium hydroxide (NaOH) solution as required. To determine the optimal dose of sorbent, a wide range of adsorbent masses (0.6; 0.8; 1; 2; 3; 4; 5; 6.2; 7; 8 g) were shaken in 40 ml of an arsenic solution (5 mg/L). The samples were agitated with rotary shaker (Retsch, Berlin) at 200 rpm for 24 h. After filtration through a 0.45 μm cellulosic acetate film, the As (III) concentration of the filtered solutions was analyzed with Optical Emission Spectrometer OPTIMA 2100 Dual View (ICP-OES 2100 DV). The As (III) adsorbed percentage was calculated using this relation (1):

$$\% \text{ As}\left(\text{III}\right) \text{ adsorbed} = \frac{\left(C_0 - C_f\right)}{C_0} * 100 \tag{1}$$

The amount of As (III) adsorption at any time *t*, q_t (mg/g), was calculated according to Equation (2):

$$q_t = \frac{\left(C_0 - C_f\right)}{m} * V \tag{2}$$

where:

C_0 (mg/L) = Initial arsenic concentrations

C_f (mg/L) = Equilibrium arsenic concentrations

V (L) = Volume of the As (III) solutions

m (g) = Adsorbent mass

q_t (mg/g) = Adsorption capacity.

2.3. Effect of pH on As (III) Adsorption

The effect of solution pH was carried out by adding the optimal dose of sorbent in 40 mL of As (III) solution at 5 mg/L as initial concentration at different pH values (4.0 - 10.0). These pH values were obtained by adding into each solution the required amounts of dilute nitric acid (HNO₃) or sodium hydroxide (NaOH). The mixture was agitated with a rotary shaker (Retsch, Berlin) for 12 hours at 25°C. The As (III) adsorbed percentage was calculated according to Equation (1).

2.4. Adsorption Kinetics and Effect of Initial Concentration

The adsorption kinetic study was performed for As (III) in aqueous solution at pH 7 and room temperature (25°C). Several glass vials were used to hold 40 mL As (III) aqueous solution of known initial concentration (1, 5 and 10 mg/L) and optimal dose of different adsorbents (Laterite, Sandstone and Shale), and shaken at 200 rpm for 24 hours. Samples were taken at a definite time interval and fil-

tered through a 0.45 µm cellulosic acetate film. Filtrates were analyzed to determine residual As (III) concentration.

2.5. Mathematical Modeling of Adsorption Kinetics

In the present investigation, the adsorption data were analyzed using three kinetic models: the pseudo-first-order, pseudo-second-order kinetic and the intraparticle diffusion models.

The first-order Lagergren's equation is used to determine the rate of the reaction. The equation is:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1}{2.303} * t \qquad (3)$$

where K_1 = constant rate of adsorption, q_e = amount of solute adsorbed (mg/g) at equilibrium, q_t = amount of solute adsorbed (mg/g) at any time t and t = time (min). When $\log(q_e - q_t)$ is plotted against t, and K_1 could be obtained from the slope of the straight line.

The pseudo-second-order reaction is greatly influenced by the amount of pollutant adsorbed on the material's surface and the amount of equilibrium adsorbed pollutant. The pseudo-second-order kinetics may be expressed in a linear form as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where the equilibrium adsorption capacity (q_e), and the second order constants k_2 (g/mg h) can be determined experimentally from the slope and intercept of plot t/q versus t.

The kinetic experimental results were also be fitted to the Weber's intraparticle diffusion model [16]. The rate constants of intra-particle transport (K_d) can be calculated from the Weber Morris equation. The equation is:

$$q\left(t\right) = K_d t^{0.5} + C \qquad (5)$$

where, $q(t)$ = amount of As (III) adsorbed in mg/g, t = time in minute.

3. Results and Discussion

3.1. Adsorbent Dose

A batch test was performed to determine the best sorbent concentration. **Figure 1** shows the effect of adsorbent dose on As (III) removal percentage. One could observe that As (III) removal efficiency increased adsorbent dose increase. The optimum percentage was 88%, 83% and 76% for an optimal concentration of 50 g/L laterite, 75 g/L sandstone, and 145 g/L shale, and it increased up to more than 90% for adsorbent dose of 200 g/L. Gupta *et al.* [17] showed that the higher the adsorbing surface is provided over the amount of solute adsorbed is important. However, a further increase of the adsorbent slightly affects the adsorption of As (III) due to agglutination of the adsorbent particles.
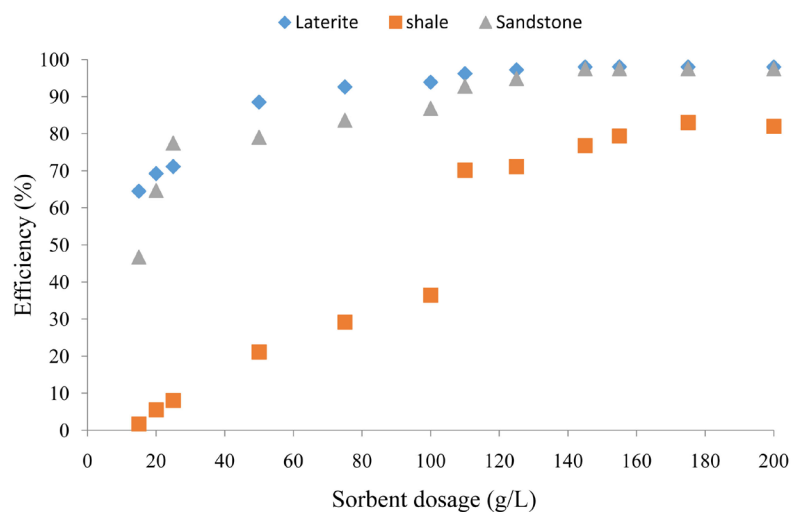
Figure 1. Effect of adsorbent dose on As (III) adsorption (C_0 = 5.0 mg/L, pH: 7, agitation speed: 200 rpm).

3.2. Adsorption Kinetics Measurement

The effect of contact time on the amount of arsenic adsorption by laterite, sandstone and shale was studied using optimal mass of the adsorbents, at pH 7.0 with initial concentration of As (III) at 5 mg/L (**Figure 2**). The As (III) adsorption capacity increased from 0.053 mg/g to 0.076 mg/g laterite and decreased thereafter. A similar effect, was observed for sandstone and shale, where the As (III) adsorbed capacity increased from 0.035 mg/g to 0.050 mg/g for the sandstone and 0.012 mg/g to 0.020 mg/g for the shale. The As (III) adsorption on the laterite, sandstone and shale occurred quickly in the initial phase of the experiment. This could be due to the availability of a large number of adsorption sites on the surface of the material. Maximum As (III) adsorption was observed after a stirring times of 5, 3 and 8 h for laterite, sandstone and shale respectively.

3.3. Effect of Initial Concentration

Figures 3-5 present respectively the effect of initial arsenic concentration on laterite, sandstone and shale adsorption capacity. The As (III) adsorption capacity increased with increasing initial arsenic concentration (**Table 1**). This is probably due to the availability of large vacant adsorbent sites and a high concentration gradient [18]. For concentrations below 5 mg/L, after treatment, residual arsenic was less than 0.01 mg/L which is the standard of WHO for drinking water.

3.4. pH Effect

Arsenic adsorption efficiency by laterite, sandstone and shale versus pH is reported in **Figure 6**. The arsenic adsorption capacity of the three adsorbents increased in the pH range of 4 - 7. The pH that allows the maximal adsorption is 7 for the laterite and 6 for the two other absorbents. Beyond 6, the adsorption decreased from 71.27% to 45.88% for shale. However, the Arsenic rate retention
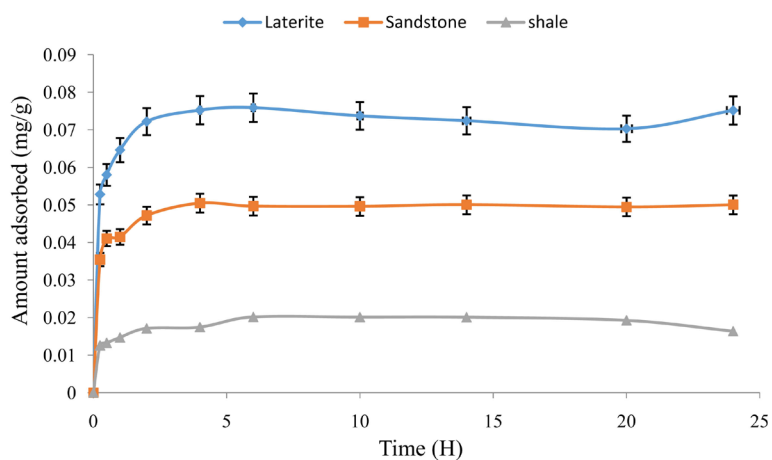
Figure 2. Effect of contact time on the adsorption of As (III) [Conditions: As (III): 5 mg/L, pH: 7, agitation speed: 200 rpm].
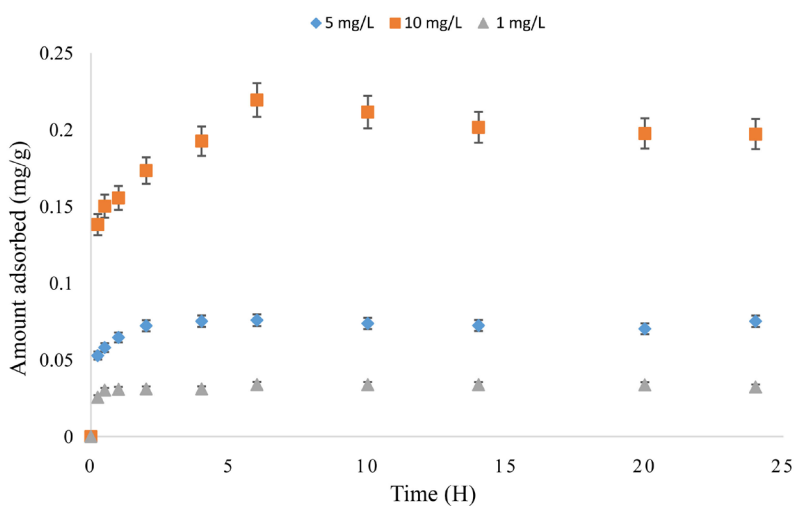

Figure 3. Effect of reaction time on As (III) adsorption at various initial concentrations by laterite.
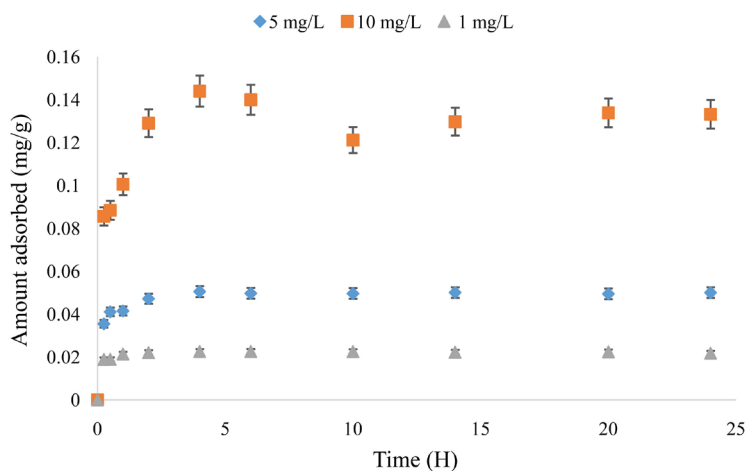

Figure 4. Effect of reaction time on As (III) adsorption at various initial concentrations by sandstone.
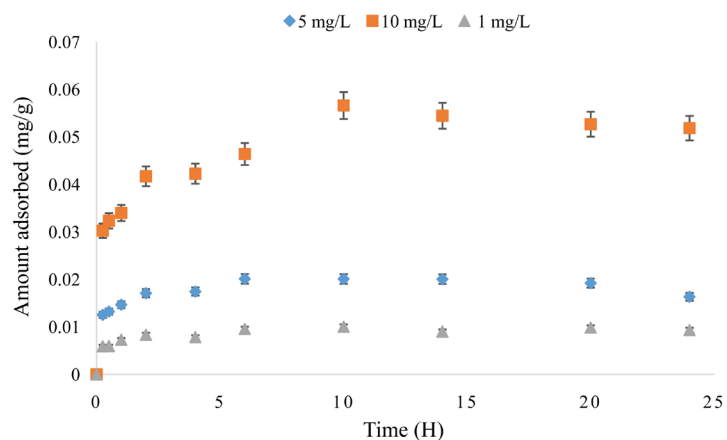
345

Figure 5. Effect of reaction time on As (III) adsorption at various initial concentrations by shale.
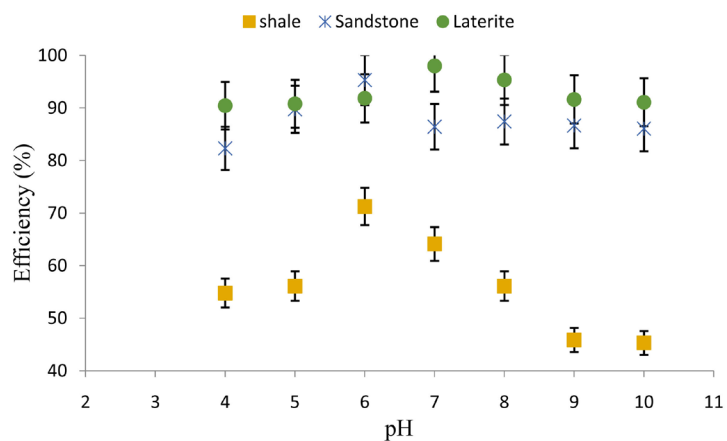

Figure 6. As (III) ion removal versus pH onto laterite, sandstone and shale. Experimental conditions: initial arsenite concentration = 5 mg/L, adsorbent amount = 50, 75 and 145 g/L respectively for laterite, sandstone and shale, pH range = 4 - 10, shaking time = 12 h, temperature = 25°C - 30°C.

Table 1. Kinetic parameters As (III) adsorptions by laterite, sandstone and shale.

Materials	Experimental parameters		Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intra-particle diffusion model		
	C_o (mg/L)	$q_{e\,exp}$ (mg/g)	$q_{e\,cal}$ (mg/g)	K_1 (h^{-1})	R	$q_{e\,cal}$ (mg/g)	K_2	R	K_d (mg/h$^{1/2}$g)	C	R
Laterite	1	0.034	0.001	0.107	0.422	0.031	1809.901	0.998	0.001	0.028	0.725
	5	0.076	0.005	0.059	0.322	0.073	262.424	0.998	0.003	0.060	0.673
	10	0.219	0.028	0.039	0.219	0.199	172.932	0.998	0.013	0.151	0.757
Sandstone	1	0.022	0.001	0.049	0.277	0.022	1331.689	0.999	0.0006	0.020	0.635
	5	0.050	0.003	0.103	0.534	0.050	203.402	0.999	0.002	0.040	0.769
	10	0.144	0.019	0.034	0.243	0.133	47.420	0.998	0.009	0.098	0.673
Shale	1	0.010	0.002	0.092	0.592	0.009	355.900	0.997	0.0008	0.006	0.837
	5	0.020	0.002	0.073	0.277	0.017	240.955	0.992	0.001	0.014	0.672
	10	0.056	0016	0.092	0.643	0.053	40.896	0.998	0.005	0.030	0.901

decreased from 98.01% to 91.62% and from 95.32% to 86.66% on laterite and sandstone respectively. The adsorbents surfaces are highly protonated and As (III) mainly exists neutral form H_3AsO_3. The Arsenic adsorption of hydrous iron and/or aluminium oxide of adsorbents surface is mainly by ligand exchange. The ligand exchange is envisaged like Stumm [19].

$$MOH(s) + H_3AsO_3(aq) \rightarrow MH_2AsO_3 + H_2O$$
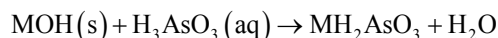
where, M as iron or aluminium.

The Point of Zero Charge (PZC) of laterite is 6.8 and the PZC of sandstone is 4.3 - 5.6 [14]. At pH greater than the PZC, adsorbent surface is negatively charged and arsenite adsorption decreases due to electrostatic repulsion. Similarly, maximum adsorption was observed for As (III) adsorption in the pH range 6 - 7 on activated coals [20].

3.5. Mathematical Modeling of Adsorption Kinetics

Kinetic models including the pseudo-first-order model of Lagergren, the pseudo-second-order model of Richie and intra-particle diffusion models were tested for experimental results simulation.

3.5.1. Pseudo-First-Order Model

The fact that the plot would be found to be linear with a week correlation coefficient (**Figures 7-9**), would indicate that Lagergren's equation is not appropriate to describe the As (III) adsorption. However, it was observed that the Lagergren pseudo-first-order model did not fit well, since the calculated q_e values do not agree with the experimental q_e values (**Table 1**). This suggests that the adsorption of arsenic does not follow a real first-kinetic order.

3.5.2. Pseudo-Second-Order Model

The fraction of arsenic adsorbed using the pseudo-second-order model is presented in **Figures 10-12**. The calculated values of K_2, experimental values of q_e
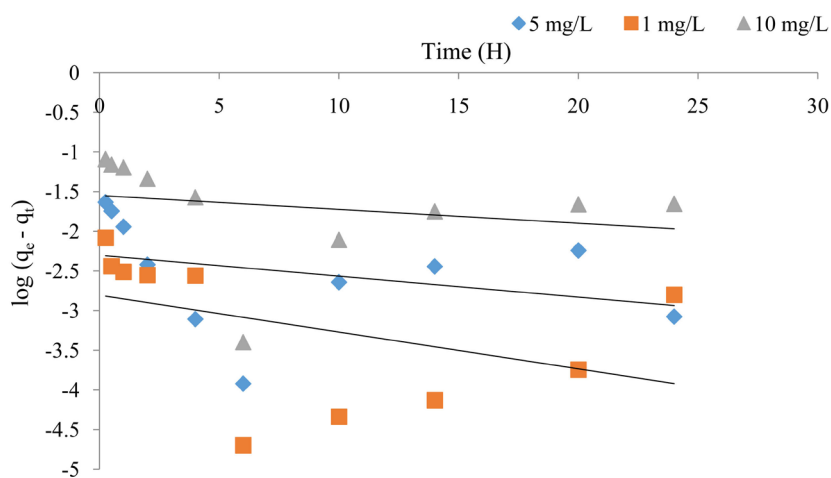

Figure 7. Plots of kinetics adsorption of arsenic (III) according to a pseudo-first-order onto laterite.
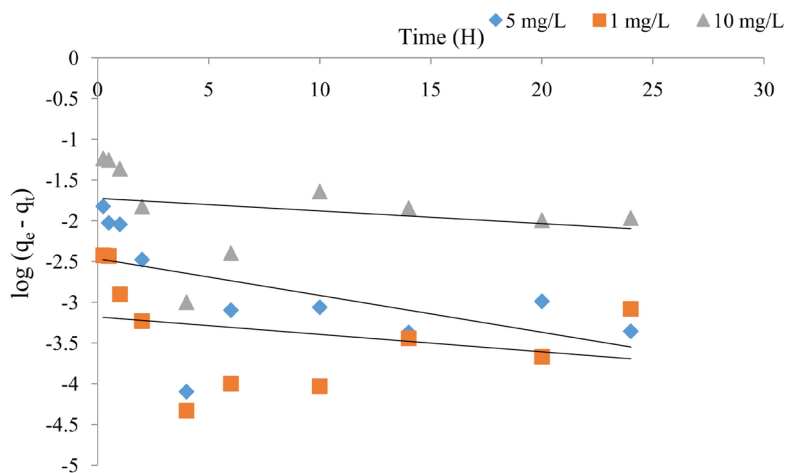
Figure 8. Plots of kinetics adsorption of arsenic (III) according to a pseudo-first-order onto sandstone.
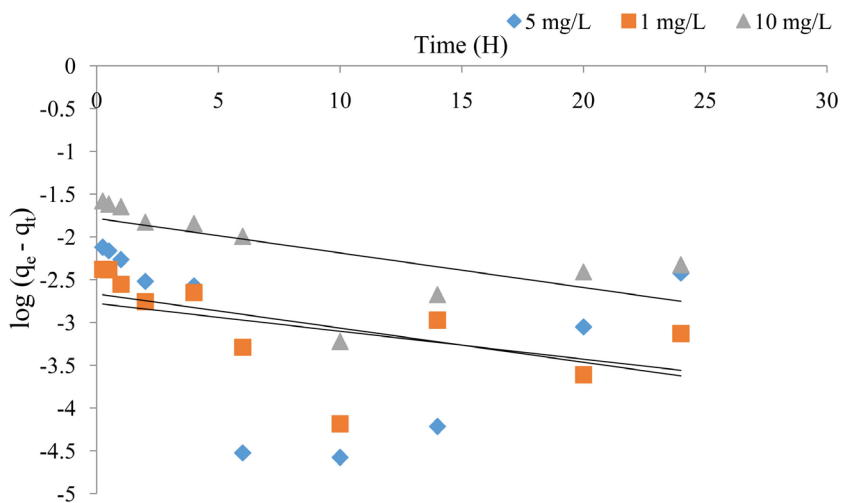

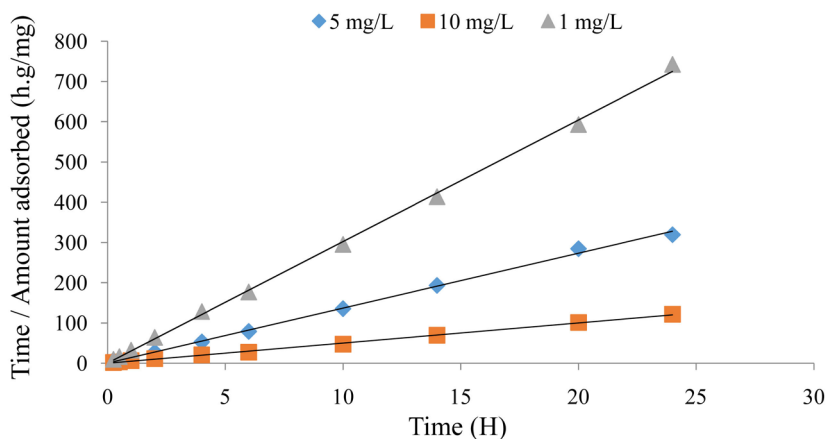**Figure 9.** Plots of kinetics adsorption of arsenic (III) according to a pseudo-first-order onto shale.

Figure 10. Plots of kinetics adsorption of arsenic (III) according to pseudo-second-order onto laterite.
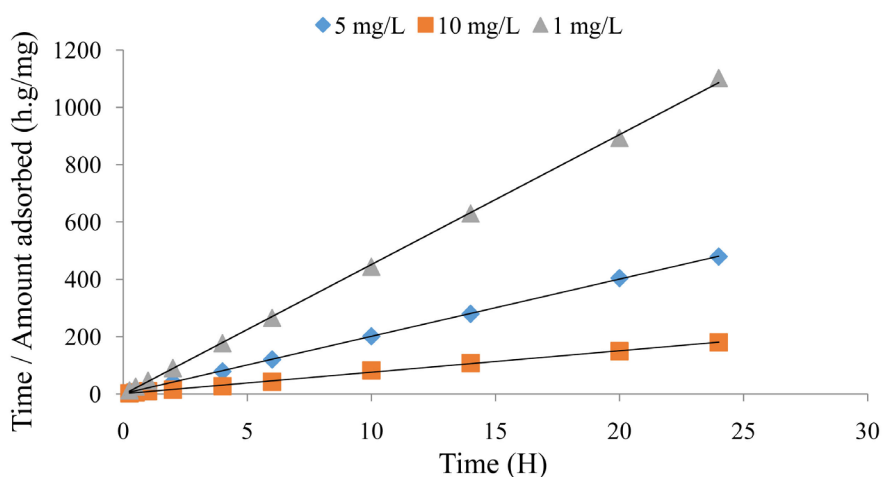
Figure 11. Plots of kinetics adsorption of arsenic (III) according to pseudo-second-order onto sandstone.
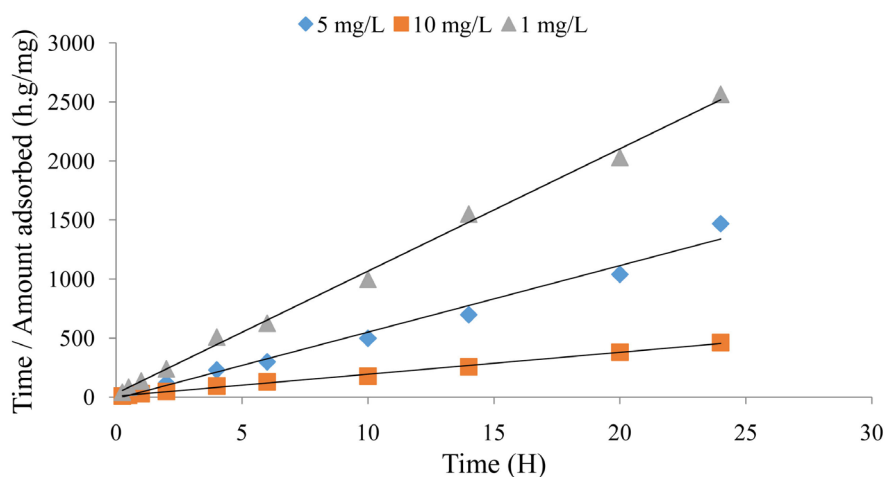

Figure 12. Plots of kinetics adsorption of arsenic (III) according to pseudo-second-order onto shale.

and the corresponding linear regression correlation coefficients R are presented in Table 1. The data showed that the R value of pseudo-second order model is greater than 0.99. In addition, the q_e (cal) obtained with the pseudo-second kinetic model, are in agreement with experimental adsorption capacity q_e (exp). The pseudo-second-order model describes better the effect of arsenic adsorption by the adsorbents, and suggests that chemisorption could be the dominant mechanism in the As (III) adsorption by laterite, sandstone and shale.

3.5.3. Intra-Particle Diffusion Models

The graphs are plotted between $q(t)$ and $t^{0.5}$ and are shown as **Figures 13-15**. K_d, the constant rates for intra-particle diffusion are determined from the slopes of the linear portion of the respective plots and are shown in **Table 1**. The linear portions of the curves do not pass through the origin, and this is an indication that the intra-particle diffusion is not the only rate controlling this step.
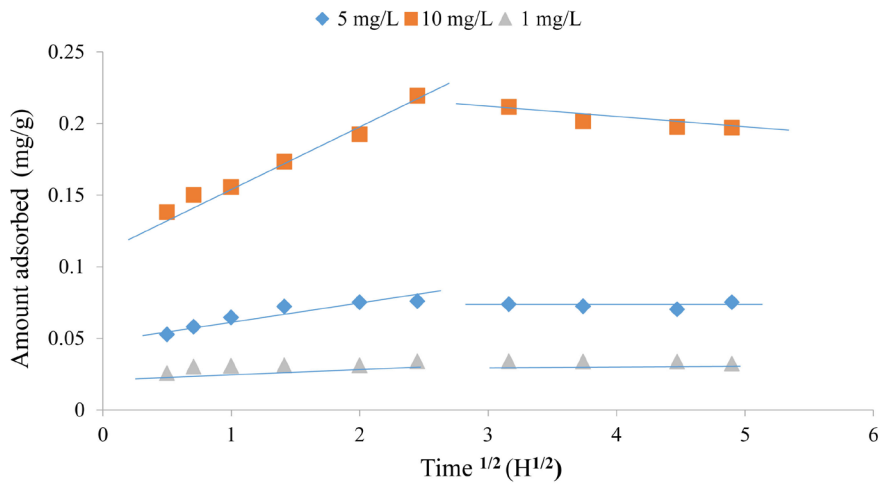
Figure 13. Plots of constant intra-particle diffusion rate for arsenic adsorption onto laterite.
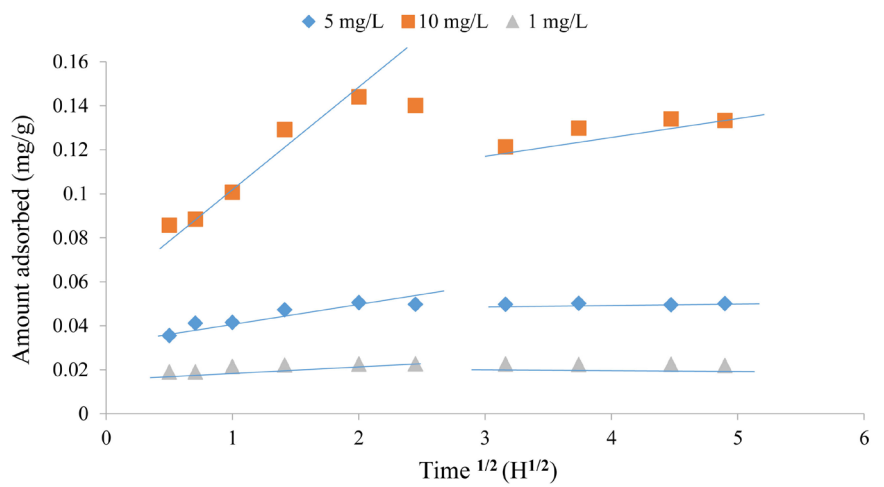

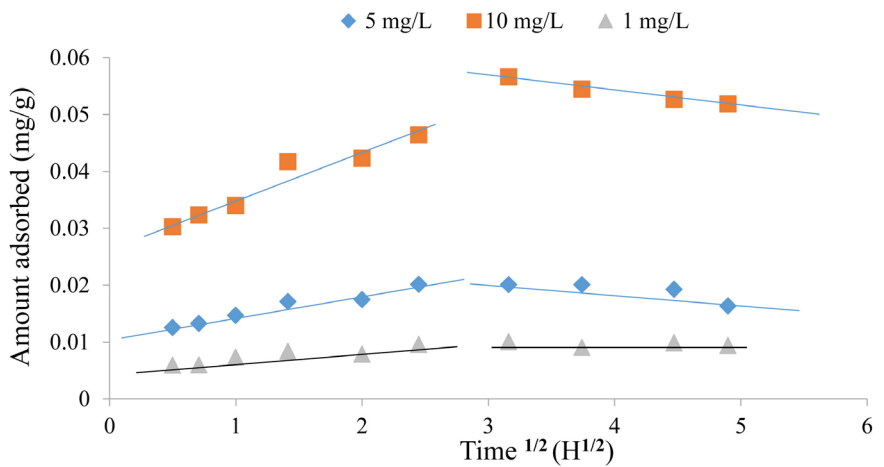**Figure 14.** Plots of constant intra-particle diffusion rate for arsenic adsorption onto sandstone.

Figure 15. Plots of constant intra-particle diffusion rate for arsenic adsorption onto shale.

The Figures 13-15 shows that all initial concentration presented two stages. The first stage could correspond to the mass transfer of the absorbed ions from the bulk solution to the adsorbents surface or instantaneous reactions and the second stage is the intra-particle diffusion on absorbents. It is appears that those intra-particles rate constant values (K_d) increased with initial As concentration. The increase of K_d with the increase of initial As concentration could be explained by the growing effect of driving force which will reduce the diffusion of As species in boundary layer and enhance to diffusion in the solid. Otherwise, the high K_d values of laterite could be related to its high porosity and specific area in relation to the sandstone and shale [15].

4. Conclusion

Laterite, sandstone and shale were successful in removing arsenic from groundwater. About 88%, 83% and 76% arsenic was removed respectively by laterite, sandstone and shale using dose of 50, 75 and 145 g/L, for an initial arsenic concentration of 5.0 mg/L. Studies revealed that for optimal operation, the pH should be set between 6 and 7. From kinetic study, it is observed that maximum adsorption occurs in five hours for the laterite, three hours for the sandstone and eight hours for the shale. The pH, contact time and initial concentration, affect significantly the As (III) absorption capacity. Water satisfying the World Health Organization (WHO) standard for drinking water for concentrations below 5 mg/L. The pseudo-second-order model better describes the adsorption of As (III) on the laterite, sandstone and shale. The adsorption process is dominated by the chemisorption.

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