Utilization of Calcined Sandstone and Calcined Laterite as an Adsorbent for the Removal of Arsenic from Water

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Abstract
Calcined sandstone and calcined laterite were tested as adsorbent at a low cost for the removal of arsenic (As) from the drinking water. The natural materials were collected in Côte d'Ivoire, washed and then dried at a temperature of 60 °C and finally calcined in an oven at the atmospheric air in several temperatures 300 °C, 400 °C, 500 °C, 600 °C and 700 °C. The study of adsorption of the arsenic was realized for the various adsorbates. It showed that the biggest efficiency of the elimination was attributed to the calcined sandstone to 300°C and 400°C for laterite during 2h with a percentage that reached 99.4 %. At this calcination temperature, a mount of arsenic in treated water, satisfying the World Health Organization (WHO) standard for drinking water at initial arsenic concentrations greater than 5 mg/L. The chemical composition of the obtained adsorbs was analyzed by X-ray diffraction, Fourier transform infrared spectroscopy (FTIR) and thermal analysis (TGA-DSC). Adsorption has been described by the pseudo-second-order model. Calcination of sandstone and laterite increases the adsorption of arsenic on the materials.

Keywords: Arsenic, calcined sandstone, calcined laterite, adsorption, temperature.

1. Introduction
Elevated concentration of arsenic (As) in soil and groundwater arising from both natural (Fields et al., 2000) source and anthropogenic activities are reported in several countries around the world (Welté & Montiel, 2004). Ingestion of arsenic leads to abdominal pain, hyper pigmentation of the skin, vomiting, diarrhea, cholera and skin, bladder, lungs, kidneys and liver cancers (Nzihou et al. (2013), Wang et al. (2014)). This injection may also cause an increase in spontaneous abortions, late fetal deaths, prematurity and low birth weight (INERIS, 2014). The most indicators sensitive of chronic exposure to arsenic are cutaneous effects, which are the earliest clinical sign of arsenic poisoning. The optimal arsenic level in drinking water should lie below 0.01 mg/L according to WHO guidelines (OMS, 2004). The works of Mangoua-Allali et al. (2015) reported arsenic levels above the WHO threshold value in well water in Akouédo, Côte d'Ivoire. There are several techniques to reduce the arsenic rate of water. However, the most popular are coprecipitation (iron or aluminum salts, lime, oxide of manganese), ion exchange (Ficklin, 1983), reverse osmosis or nanofiltration (Sato et al., 2002) and adsorption. For example, ion exchange is a simple but limited method because it requires filtering the samples to remove suspended solids, the problem of deterioration of the support and the fate of the concentrated waste obtained (Korngold et al., 2001). The use of membrane techniques such as reverse osmosis or nanofiltration makes it possible to obtain a very low residual arsenic concentration but requires pre-conditioning of the water to be treated and poses regeneration problems (Clifford & Lin, 1991). The high cost of these methods limits their use. In recent years, adsorption techniques have been quite popular, due to their simplicity as well as the availability of wide range of adsorbents. Removal of pollutants from aqueous environments onto microporous active carbon is a favorite choice because of the high adsorption capacity (Ziati et al., 2012). However the high cost and irreversible nature of adsorption makes its use limited. Several workers have used a variety of low-cost adsorbents, both natural and synthetic (Chutia et al., 2009; Kim et al., 2004). Calcined sandstone and laterite has been used in this study, to remove arsenic. We present firstly, our obtained results on the characterization calcined materials. In the second part, we present results concerning the adsorption of arsenic on these three materials. The extent of adsorption was investigated as a function of contact time, initial concentration and solution pH.

2. Material and methods
2.1. Adsorbent
In this research, Sandstone and Laterite used are local natural materials collected respectively at Akouedo and Sinematialy in Ivory Coast. These materials were washed several times to remove earthy matter and finally rinsed with distilled water. Then, the samples were crushed and sieved to have a desired particles size (less than 250 µm) using a Saulas NF.X 11.501 sieve.
2.1. Adsorbate
Arsenic stock solution was prepared by dissolving reagent-grade As (III) of 99.5% purity into deionized water. Working solutions containing arsenic were prepared by dissolving appropriate amount of arsenic from stock solutions in well water (Nemade et al., 2009). Well water analysis showed that pH varied from 6.3 to 6.6. Experiments were performed at ambient temperatures (25°C).

2.2. Effect of Calcination temperature: Optimal temperature
Sandstone and laterite were calcined at different temperatures, such as 300°C, 400°C, 500°C, 600°C and 700°C for 2h, and used to conduct the adsorption of arsenic in a batch at room temperature (25°C). The adsorption process was carried out by using 40 ml of groundwater containing arsenic in a 500 mL glass vials. The glass vials was placed in a speed-controlled stirrer at 200 rpm. Initial arsenic concentrations is 5 mg/L. Adsorbent dosage was 3g of sandstone and 2g of laterite (Koua-Koffi et al., 2018) and pH of water was maintained at 7 by adding HNO₃ or NaOH. In order to remove the suspended solid particles, after 24h of adsorption, the treated water was filtered by 0.45 µm cellulose acetate film. Arsenic concentration was analyzed using an Optical Emission Spectrometer OPTIMA 2100 Dual View (ICP-OES 2100 DV). The arsenic adsorbed percentage was calculated using this relation (1):

\[
\% \text{ As (III) adsorbed} = \left( \frac{C_0 - C_f}{C_0} \right) \times 100
\]

where \( C_0 \) and \( C_f \) are the initial Arsenic concentration and the final concentration of As in the solution at the time \( t \) (mg/L).

2.3. Characterization of adsorbent
Calcined sandstone and laterite have been characterised by Fourier Transform Infrared (FTIR) spectroscopy (Bruker Alpha-p) in the spectral range of 400 and 4000 cm\(^{-1}\), by X-ray diffraction (XRD) to identify the mineralogical phases, and by thermal analysis (TGA-DSC).

2.4. Adsorption studies
2.4.1. Adsorption kinetics and effect of initial concentration
The adsorption kinetic study was performed for arsenic in aqueous solution at pH 7 and room temperature (25°C). Several glass vials were used to hold 40 mL arsenic aqueous solution of known initial concentration (1, 5 and 10 mg/L) and 2g of calcined laterite, 3g of calcined sandstone and shaken at 200 rpm for 24 hours. The samples were withdrawn from the shaker at intervals from 15 min to 24 h, filtered and the supernatants were analyzed by Optical Emission Spectrometer OPTIMA 2100 Dual View (ICP-OES 2100 DV). The quantity of arsenic adsorption at any time \( t \), \( q_t \) (mg/g), was calculated according to relation (2):

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

where \( C_0 \) is the initial As concentration (mg/L), \( C_t \) is the final concentration of arsenic in the solution after equilibrium is attained (mg/L), \( V \) is the volume of the arsenic solution (L) and \( m \) is the weight of the adsorbent (g) used.

2.4.2. Effect of pH on Arsenic adsorption
The effect of solution pH was carried out by adding the optimal dose of sorbent in 40 mL of arsenic solution at 5 mg/L. The pH (4.0–10.0) was adjusted by adding a few drops of dilute NaOH or HNO₃. pH values were controlled by a pH meter. The mixture was agitated with a shaker for 12 hours at 25°C. The As adsorbed percentage was calculated according to relation (1).

2.5. Mathematical modeling of adsorption kinetics
Arsenic 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 relation (3) is:

\[
\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t
\]

where \( K_1 \) = rate constant of adsorption, \( q_e \) = amount of solute absorbed (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 pollutant adsorbed at equilibrium. The pseudo second order kinetics may be expressed in a linear form as Ho (2006) relation (4).

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

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 fitted to the Weber's intraparticle diffusion model. The rate constants of intra-particle transport ($K_d$) can be calculated from the Weber Morris (1963) equation. The relation (5) is:

$$q(t) = K_d t^{0.5} + C$$

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

2.6. Statistical tests
Statistical tests were performed using the Rstudio 3.2.2 software. The wilcoxon test (non-parametric tests) was applied to examine the variability of materials. The threshold of significance of these different tests is 0.05.

3. Results and discussion
3.1. Effect of Calcination Temperature on the Adsorption of Arsenic
The adsorption of arsenic using calcined sandstone and laterite at different temperatures ranging from 300 °C to 700 °C, showed a high percentage of arsenic removal (Table 1). The arsenic removed from calcined sandstone decreases after 300°C, hence the percentage of adsorption which goes from 99.76% to 80.57% for initial arsenic concentration of 5 mg/L. For calcined laterite, a decrease in the percentage of removal of arsenic after 400°C (99.8% to 85.81%). These results show that calcination at a high temperature reduces the adsorption of arsenic. Its suggested that calcination at a high temperature may affect the physical structure or chemical components of the adsorbent, or both (Valix & Cheung, 2002) and reduce adsorption. Four hundred degrees celsius is the best calcination temperature of laterite and 300°C for Sandstone for the adsorption of arsenic satisfied the WHO standard, which states that the maximum arsenic concentration in drinking water must be lower than 0.010 mg/L. This calcination temperature of laterite is similar to those of Nguyen et al. (2011). However, for these authors, the calcination was made during 4h while our study shows that 2h is sufficient to have the same efficiency from where an economy of energy and time. The efficiency of this material at this temperature probably results from the different transformations produced during heating. Ruan & Gilkes observed a good adsorption capacity for calcined laterite at 220°C. This difference in temperature could be explained by the origin of the materials. Indeed, temperatures to achieve transformations in the property of the materials can vary according to the origin of the materials (Issiakou, 2016).

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Initial concentration of As (mg/L)</th>
<th>Concentration after treatment (mg/L)</th>
<th>Adsorption percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laterite</td>
<td>4.23</td>
<td>0.030</td>
<td>99.286</td>
</tr>
<tr>
<td></td>
<td>4.23</td>
<td>0.008</td>
<td>99.80</td>
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<td></td>
<td>4.23</td>
<td>0.014</td>
<td>99.661</td>
</tr>
<tr>
<td></td>
<td>4.23</td>
<td>0.095</td>
<td>97.754</td>
</tr>
<tr>
<td></td>
<td>4.23</td>
<td>0.6</td>
<td>85.815</td>
</tr>
<tr>
<td>Sandstone</td>
<td>4.23</td>
<td>0.010</td>
<td>99.76</td>
</tr>
<tr>
<td></td>
<td>4.23</td>
<td>0.017</td>
<td>99.59</td>
</tr>
<tr>
<td></td>
<td>4.23</td>
<td>0.021</td>
<td>99.484</td>
</tr>
<tr>
<td></td>
<td>4.23</td>
<td>0.224</td>
<td>94.704</td>
</tr>
<tr>
<td></td>
<td>4.23</td>
<td>0.822</td>
<td>80.567</td>
</tr>
</tbody>
</table>

3.2. Characterization of adsorbents
The mineralogical constitution of calcined sandstone and calcined laterite sample was examined by X-ray diffraction (XRD). As it is shown in figure 1, the calcined laterite contained goethite (its peaks at 4.16 and 2.43 Å), quartz (2.45; 2.27 and 1.67 Å), hematite (2.71; 2.51; 2.20 and 1.69 Å), gibbsite (4.86; 4.37; 3.18; 2.45; 2.39 and 1.98 Å) and kaolinite (7.18; 3.55; 2.51; 2.13; 1.82 and 1.67 Å). These minerals are commonly present in laterites. According to Gidigasu, (1971), the mineralogy of these minerals is linked to its genesis and the laterite of Ivory Coast is derived from the alteration of granite and phylliths. While calcined Sandstone component were goethite (4.98, 2.58 and 1.72 Å), and hematite (2.67, 2.51 and 2.24 Å). The predominant mineral of calcined Sandstone is quartz (4.27; 3.34; 2.46; 2.27; 2.13; 1.98; 1.82 and 1.67 Å).
Figure 1. XRD patterns of calcined sandstone and calcined laterite

Figure 2 presented the FTIR spectra of calcined sandstone and calcined laterite in the spectral range of 4000 and 400 cm\(^{-1}\). The analysis of the FTIR of calcined laterite (Figure 2b) showed 3695, 3625 and 912 cm\(^{-1}\) bands due to the vibrations of the OH and SiO \((1117, 1031, 1008 \text{ cm}^{-1})\) groups characteristic of kaolinite (Prado et al., 2007). In addition, the bands at 3535; 3469; 3412; 800 and 783 cm\(^{-1}\) can be attributed to gibbsite. The presence of low intensity bands between 1000 and 2000 cm\(^{-1}\). In this interval the bands 2000; 1868 and 1819 cm\(^{-1}\) can be attributed to harmonics and combinations of orthosilicates. The adsorbed water and carbonates are respectively represented by the strips 1667 and 1363.

For sandstone (Figure 2a), the 2135 band is thought to be due to the asymmetric elongation vibrations of carbonates related to calcite. The other bands to 1985; 1651, 1654, 1079, 1087, 1042 could be related to the Si-O bonds of quartz and its harmonics (Farmer, 1974; Igo et al., 2006). The 3185 cm\(^{-1}\) band can be attributed to the OH elongation vibrations of the goethite network after Rochester & Topham (1979), Mendelovici et al. (1979). As for the band 893 and cm\(^{-1}\), it is attributed to the OH deformation vibrations linked to goethite. Bands at 3702; 3695 and 3651 cm\(^{-1}\) of low intensities are known to be characteristic bands of kaolinite according to Schroeder (2002). Bands at 798; 780; 695 and 696 are characteristic of quartz. And the 695 and 696 band attributable to the Si-O deformation vibration accounts for the crystallinity of the quartz contained in this material (Saika et al., 2008).

Figure 3 shows the TGA-DSC of sandstone and laterite. The treated samples have 3 large areas of distinct mass loss and endothermic peaks: a first loss of mass is about 1.70% for sandstone and 1.44% for laterite. This loss is marked by an endothermic peak that occurs around 52°C and 45°C respectively for sandstone and laterite. The second weight loss is from the order of 0.14% for sandstone, 4.05% for laterite. Endothermic peaks are recorded around 267 °C and 283°C for laterite. This phase, difficult to identify for sandstone, is around 200 ° C. The third loss of mass is 5.10% with a large endothermic peak observed around 493 °C for laterite. For sandstone, the mass loss is 0.25% and 0.84% respectively. The endothermic peak is around 569°C. Endothermic peaks and loss of mass which marks the departure of hygroscopic and zeolitic water (Carlos et al., 2004), transformation of goethite into hematite by dehydroxylation (Frost & Vassallo, 1996).
Figure 2. FTIR spectra of calcined sandstone (a) and calcined laterite (b)
3.3. Effect of contact time and initial concentration

The results of Kinetic studies with different concentrations initial (1-10 mg/L) are shown in Figure 4. As shown in these curves, a rapid arsenic adsorption occurred during the first minutes, indicating an affinity between arsenic and sandstone, shale and laterite surface. This phase would be dependent on easily accessible sites such as external surfaces of particles and macro-pores, or would correspond to the fixation of arsenic ions at the most reactive sites (instant adsorption) (Coulibaly et al., 2016). After approximately 3h and 5 h, the adsorbed amount was stable suggesting a gradual equilibrium respectively from calcined sandstone and laterite. The second phase is slower and stationary, it would be characteristic of a retention of arsenic after diffusion of ions in the meso-
and micropores (gradual adsorption). Therefore a time of 3h and 5h was chosen for the following experiments concerning calcined sandstone and laterite. Adsorption capacity increases by increasing the initial concentration (1-10 mg/L). The increase in adsorption capacity with the initial concentration could be attributed to the high concentration of arsenic, which provided a greater driving force for the transfer process to overcome mass transfer resistance. A similar observation was made by Sarkar et al. (2006) in the interaction of fluoride with crude laterite. The adsorption capacity of arsenic with the calcined materials of this study is greater than that of the same natural materials used by Koua-Koffi et al. (2018). The efficiency of calcined adsorbents is probably due to the activation that widened the pore diameter and created new ones. The heating would have induced the appearance of defects in the structure of the material, including voids formed by the departure of the water and the formation of micropores of the nanometer order, associated with the change of volume necessary for the formation of goethites partially dehydroxylated. This mechanism has been demonstrated by Ruan & Gilkes, (1996). Indeed, these authors have shown that partially dehydroxylated goethites are composed of microporous mixtures of goethite and small crystal hematite with a larger surface area so as to promote a high adsorption of arsenic. The amount of arsenic adsorbed on calcined laterite was lesser compared to the other matrix calcined (Test T p <0.05). Laterite had the best efficiency and was followed by sandstone.

![Figure 4. Effect of contact time on the adsorption of Arsenic by calcined sandstone (a) and laterite (b)](image)

**3.4. Effect of pH**

The chemical characteristics of both adsorbent and adsorbate could be varied with pH. The pH of the solution affects the degree of ionization and speciation of various arsenic which subsequently leads to a change in the
kinetics reaction and equilibrium characteristics of the adsorption process. The experimental results for the arsenic adsorption on the calcined materials are shown in Figure 5. The figure shown the adsorption capacities increased with increasing pH. For all adsorbents studied, the optimal pH of adsorption is 6.0. However, with a further increase in pH, percentage removal decreases. The decreases of the percentage can be attributed to the Point of Zero Charge (PZC) of the laterite which is 6.8 and for sandstone is 4.3- 5.6 (Coulibaly et al., 2016). At pH higher that the PZC, calcined sandstone and laterite surface is negatively charged and arsenic adsorption becomes less due to repulsion of similar charge, as arsenite exists as anion in that pH range (Maiti et al., 2011). Similarly maximum adsorption was observed for As (I II) adsorption on iron-oxide coated sand in the pH range 7-7.6 (Gupta et al., 2005). Arsenic adsorption at this pH is of the same order as Wilkie & Hering, (1996) where the As (III) adsorption on hydroxide ferric increased with pH up to maximum adsorption at pH 7.

![Figure 5. Arsenic removal as a function of pH reactions](image)

3.5. Mathematical modeling of adsorption kinetics
The process of arsenic removal from aqueous phase by calcined sandstone and laterite could be modeled by pseudo-first-order kinetics (reversible or irreversible) or pseudo-second-order kinetics and intra-particle diffusion models.

3.5.1. Pseudo-first-order model
Figure 6 show the fraction of arsenic adsorbed calculated with the pseudo-first-order. The correlation coefficients for calcined sandstone and laterite are higher than 0.78, and q_e values do not agree with the experimental q_e values (Table 2). This shows that the transfer of arsenic can not be described by a first order law. In other words, the rate of reaction does not depend solely on the concentration of arsenic in solution, which indicates that the adsorption of arsenic is not an ideal pseudo-first-order reaction.
3.5.2. Pseudo-second-order model

The plot of \( \frac{t}{q_t} \) versus \( t \) is shown in Figure 7. For this adsorbents, the calculated values of \( K_2 \), experimental values of \( q_e \) and the corresponding linear regression correlation coefficients \( R \) are presented in Table 2. The data showed that the \( R \) value of pseudo-second-order model is more than 0.99. More important, 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. Conformity to the pseudo-second order model suggests that chemisorption is the dominant mechanism in arsenic retention on the two used laterite. Similar kinetics have been reported by Zehhaf et al. (2015) for the adsorption of arsenic on montmorillonite.
3.4.3. Intra-particule diffusion models

The graphs are plotted between \( q(t) \) and \( t^{0.5} \) and are shown as Figure 8. \( K_d \) the rate constant for intra-particle diffusion are determined from the slopes of the linear portion of the respective plots and are shown in Table 2. The linear portions of the curves do not pass through the origin, indicate that the intraparticle diffusion is not the only rate controlling this step. The Figure 8 shows that only 10 mg/L initial concentration of the materials has two stages. Intraparticule rate constant values \( (K_d) \) increased with initial As concentration. Concerning, intra particle diffusion, the first stage could correspond to the mass transfer of the adsorbed ions from the bulk solution to the adsorbents surface or instantaneous reactions and the second stage is the intraparticule diffusion on adsorbents (Vaghetti et al., 2009). It is found that those intraparticule 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 (Coulibaly et al., 2016).
Figure 8. Plots of intra-particle diffusion rate constants for arsenic sorption onto calcined sandstone (a) and laterite (b).

Table 2. Kinetic parameters arsenic adsorption by calcined sandstone and calcined laterite

<table>
<thead>
<tr>
<th>Experimental parameter</th>
<th>Pseudo-first-order kinetic model</th>
<th>Pseudo-second-order kinetic model</th>
<th>Intra-particle diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( C_0 ) (mg As/g)</td>
<td>( q_{e,exp} ) (mg As/g)</td>
<td>( k_1 ) (h(^{-1}))</td>
</tr>
<tr>
<td>Laterite</td>
<td>1</td>
<td>0.036</td>
<td>0.0226</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.1</td>
<td>0.0519</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.24</td>
<td>0.0773</td>
</tr>
<tr>
<td>Sandstone</td>
<td>1</td>
<td>0.0024</td>
<td>0.0196</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.067</td>
<td>0.0423</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.16</td>
<td>0.0575</td>
</tr>
</tbody>
</table>

Conclusions
This work focuses on the study of the adsorption capacity of the arsenic on calcined rock particles at different temperatures. Arsenic is an inorganic pollutant and highly toxic at high doses. Characterization of our adsorbates showed that the calcination resulted in a change phase. The calcination of sandstone and laterite at 300°C and 400°C during 2h widened the pore diameter and created new ones. She induced the appearance of defects in the
structure of the material. The study of the kinetics was performed in order to understand and explain the arsenic adsorption mechanism on the calcined sandstone and laterite. After calcination of materials, adsorption capacity was increased compared to uncalcined sandstone and laterite. This study follows the pseudo-order model 2, adsorption of arsenic on these materials is likely governed by chemical interactions and then one can conclude, heterogeneity of the binding sites without any interaction between the adsorbed species. This work shows that the calcination of sandstone and laterite is a very interesting optimization setting for the treatment of drinking water polluted with the arsenic.

References


