



ARSENIC, NICKEL AND LEADREMOVAL FROM UNDERGROUND WELLS BY ADSORPTION ON LATERITE SOIL

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Abstract:

The pollution by heavy metal in the environment, particularly groundwater, constitutes an environmental problem and health in Côte d'Ivoire. Among methods used for removal heavy metals, adsorption by natural absorbent such as a laterite is effective and cheap when compared to other methods. So, this study evaluates the laterite reactor performance for effective removal of heavy metals viz., arsenic (As), nickel (Ni) and lead (Pb) from real-life groundwater. And adsorption of heavy metals was performed with laterite of different particle sizes, viz. coarse grain size of laterite (LRCOG) and laterite granules (LRG). The results obtained showed that the percentages of removal of heavy metal are higher than the size of the laterite. As, Ni and Pb removal are $98.3 \pm 0.4\%$, $99.2 \pm 0.2\%$ and $96.1 \pm 1.1\%$ respectively in LRCOG effluents. With the laterite in form of granules, percentage removal were of $98.6 \pm 0.3\%$ for As that of the Ni is of $99.7 \pm 0.2\%$ and $97.9 \pm 0.5\%$ for Pb. The adsorption of heavy metal on the two types of laterite particle size is in the same order of effectiveness: Ni>As>Pb.

Keywords: Adsorption On Laterite; Arsenic; Côte d'Ivoire; Lead; Nickel; Well Water.

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1. Introduction

Arsenic (As), nickel (Ni) and lead (Pb) are heavy metals whose natural content in the soil can vary from very small proportion, which is qualify as trace element with an excessively high concentration found in soils (Garret, 2000).As, Ni and Pb are non-biodegradable toxic heavy metal (Ilavský and Barlokobá, 2012; Alhawas, Alwabel, Ghoneim, Alfarraj and Sallam 2013).These metals have been discharged into the environment as industrial wastes causing serious problem of soil and water pollution (Tchobanoglous, Burton and Stensel, 2003; WHO, 2004).The main source of heavy metals pollution in the water came from human activities (Nkhuwa, 2003; Collin and Melloul, 2003; Cissé, Faye, Wohnlich and Gaye, 2004). The contamination of underground sources of drinking water by heavy metals, causes toxic and

carcinogenic effects on human beings. For example in India and Bangladesh, this causes nearly 100 million people to be affected by As related diseases (Saha, Dikshit, Bandyopadhyay and Saha, 1999).

In drinking water, the maximum permissible limit according WHO guidelines are 0.01 mg/L for As and Pb, and 0.07 mg/L for Ni. In Côte d'Ivoire, Koua-Koffi (2014) shows that the concentrations of As, Ni and Pb in many existing wells providing drinking water exceed over values. These wells are situated in M'badon village near Akouédo landfill in Abidjan district. Thus a cost-effective technique for arsenic, nickel and lead removal providing a safe drinking water is an urgent need. Many methods exist for removing heavy metals, including ion exchange, precipitation, ultrafiltration, and adsorption (Lenoble, 2003). Among these methods, adsorption by natural adsorbent such as a laterite is effective and cheap when compared to other methods (Altundogan, Altundogan, Tümen and Bildik, 2002). Natural laterite is a composite material of iron, aluminum and silicon (Maji, Paland Pal, 2006). In Côte d'Ivoire, the laterite soil occurs very widely in several towns of Côte d'Ivoire (e.g. Sinémentalé in the north, Bouaké in the middle, Abengourou in the south-east and in the way Abidjan-Adzopé) (Zondje, 2008). All these facts prompted the present investigators to evaluate the possibility of laterite soil to be used as a potential adsorbent for arsenic, nickel and lead removal from real sample.

Studies were conducted in rural area using real-life groundwater sample collected from M'badon village affected area by As, Ni and Pb. Concentrations of these heavy metals in drinking water exceed WHO guidelines for human health protection.

The present study is intended to evaluate the laterite reactor performance for effective removal of heavy metals viz., arsenic, nickel and lead from real-life groundwater. And adsorption of heavy metals was performed with laterite of different particle sizes, viz. coarse grain size of laterite and laterite granules.

2. Materials and Methods

2.1. Study Area

The study was carried in M'badon village at north-east of Abidjan in Côte d'Ivoire. The village is located between the northern latitudes 561 000 and 566500 m and west longitudes 396 000 and 407 000 m (Kouadio, Dongui and Trokourey, 2000). The village is near lagoon Ebrié and the Akouédo landfill which receives all the waste of the district of Abidjan.

2.2. Laterite Characteristic

The adsorbent was collected from Sinémentalé in the north Côte d'Ivoire. The material is the representative of the site chosen. The raw material did not cost anything. Detailed studies to characterize laterite have been done by Coulibaly (2014). Thus several mineralogical and physicochemical properties were determined by means of: X-ray diffraction (XRD), scanning electron microscopy (SEM), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), N₂-adsorption/desorption techniques (BET), energy dispersive x-ray spectroscopy (EDX), particle size distribution, cation exchange capacity and chemical analyses by atomic

emission spectrometry (ICP-AES) and mass spectrometry (ICP-MS). The results are given in Table 1.

Table 1: Physico-chemical composition of laterite (Coulibaly, 2014)

Properties	Quantitative value
Micropores surface (m ² /g)	6
Micropores volume (cm ³ /g)	1.71
Specific surface area (m ² /g)	34.1
SiO ₂ (%)	20.18
Al ₂ O ₃ (%)	17.92
Fe ₂ O ₃ (%)	45.10
MnO (%)	0.07
MgO (%)	0.04
CaO (%)	0.05
K ₂ O (%)	0.03
TiO (%)	0.53
P ₂ O (%)	0.68
P.F. (%)	14.01
Silt (%)	96.83
Clay (%)	0.71
Sand (%)	1.16
pHzpc	6.8

The major components on laterite soil are iron oxide (45.10%), silica (20.18%) and alumina (17.92%).

2.3. Laterite Reactor Design

Laterite reactor (LR) was a process developed at the Research Unit of Biotechnology and Environmental Engineering, Nangui Abrogoua University, Côte d'Ivoire. Two similar laterite reactors were built using polyvinyl chloride (PVC) pipe. A sketch of the laterite reactor can be seen in Fig. 1. The reactor bed consisted of two layers: gravel layer (10 cm) and laterite layer (40 cm). The gravel layer consisted of stones 15/20 mm in size, a fine cloth mesh is placed on top of the layer. The gravel is found locally, washed with clean tap water at our university and dried outside in the sun. The laterite layer consisted of coarse grain size of laterite for first reactor and laterite granules for the second reactor. The first reactor is named LRCOG and the second LRG. The granulometric parameters of each laterite are summarized in Table 2. The Uniformity Coefficient (UC), Coefficient of gradation (C_k) and Sorting index (ϕ) can be respectively quantified as: $UC > 5$ indicates a well-graded soil; $UC < 3$ indicates a uniform soil; $0.5 < C_k < 2$ indicates a well-graded soil; $C_k < 0.1$ indicates a possible gap-graded soil; $\phi < 0.35$ indicates a very well sorted; $0.35 < \phi < 0.5$ indicates a well sorted; $0.5 < \phi < 0.71$ indicates a moderately well sorted; $0.71 < \phi < 1$ indicates a moderately sorted; $1 < \phi < 2$ indicates a poorly sorted; $2 < \phi$ indicates a very poorly sorted.

Each reactor was charged with 3L/d of well water from a village of M'badon.

Table 2: Granulometric parameters of laterite used

Granulometric parameters	Coarse laterite	Granules laterite
Uniformity coefficient (UC)	0.5	0.8
Average size of grain (µm)	1290	4111
Coefficient of gradation (C _k)	1.15	1.07
Sorting index (φ)	0.14	-0.14
Hydraulic conductivity (m/s)	3.51 * 10 ⁻²	2.47 * 10 ⁻¹
Characteristics	Uniform soil, very well sorted, well-graded	

2.4. Water Analysis

Samples of raw water and treated water were collected once a week during three month and analyzed. Samples were collected in sterile 0.5 L plastic bottle. The pH was measured in all water samples with a multi parameter Model C830 consort. Determination of As, Ni and Pb were realized in the laboratory using the analytical standard methods (AFNOR): NF EN ISO 15586, NF T90-112 and NF EN ISO 15586 respectively. All the results are compared with standard limits recommended by WHO.

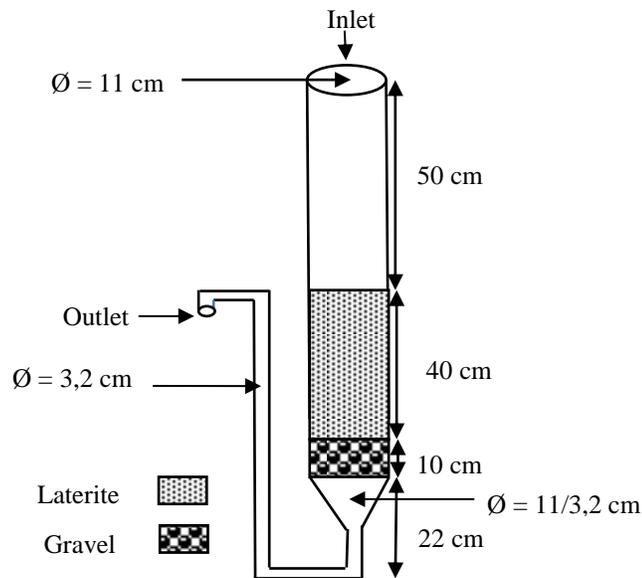


Figure 1: Sketch of the laterite reactor with measurements

2.5. Percentage of Metal Removal

The performance of the laterite reactor in reducing heavy metal is assessed by averaging the removal efficiencies of the laterite reactor over the experimental period of three month. The relation (1) is used to determine the removal efficiencies of laterite media towards each metal tested.

$$\text{Metal removal (\%)} = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

Where

C_0 : Concentration of metal in raw water (mg/L)

C: metal concentration after passing through the laterite column (mg/L)

2.6. Statistical Analysis

The normality of the data was verified using the Shapiro-Wilk test (softwareR) and homogeneity was verified by Levene's test (STATISTICA 7.1). The comparison of the variation of the parameters measured between the raw water and the effluents of LRCOG and LRG was made using the parametric test ANOVA. The post hoc t test was followed to indicate significant differences between the raw water and the effluents of LRCOG and LRG. The statistical program used for both tests was Rsoftware3.1.1 and alpha level of significance was fixed to 0.05.

3. Results and Discussion

3.1. Results

3.1.1. Ph Values of Drinking Water

In Fig. 2, the pH in effluents of LRCOG varied from 7.2 to 7.7, averaging 7.5 ± 0.14 . Effluents of LRG were between 7.3 and 7.8, averaging 7.6 ± 0.15 . These values were higher than raw water. The pH level in raw water was ranging from 5.7 to 6.5. The mean value was 5.6 ± 0.23 . A significant difference was noted between the pH of the raw water and the pH of the two effluents (test t: $p < 0.05$).

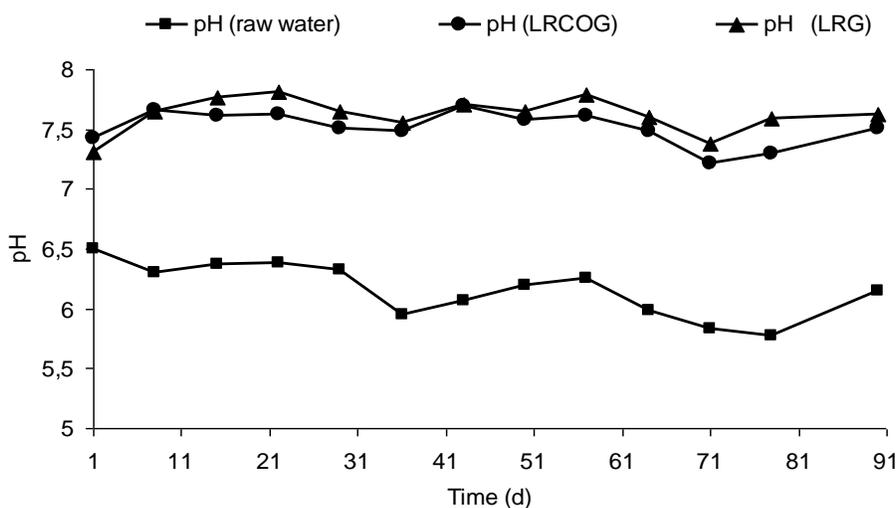


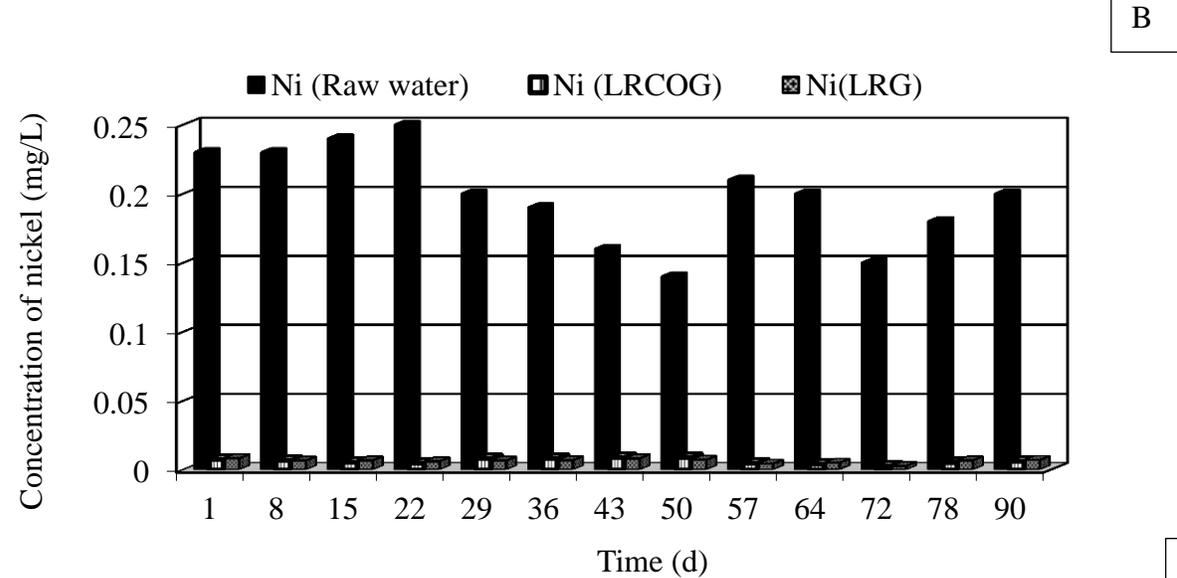
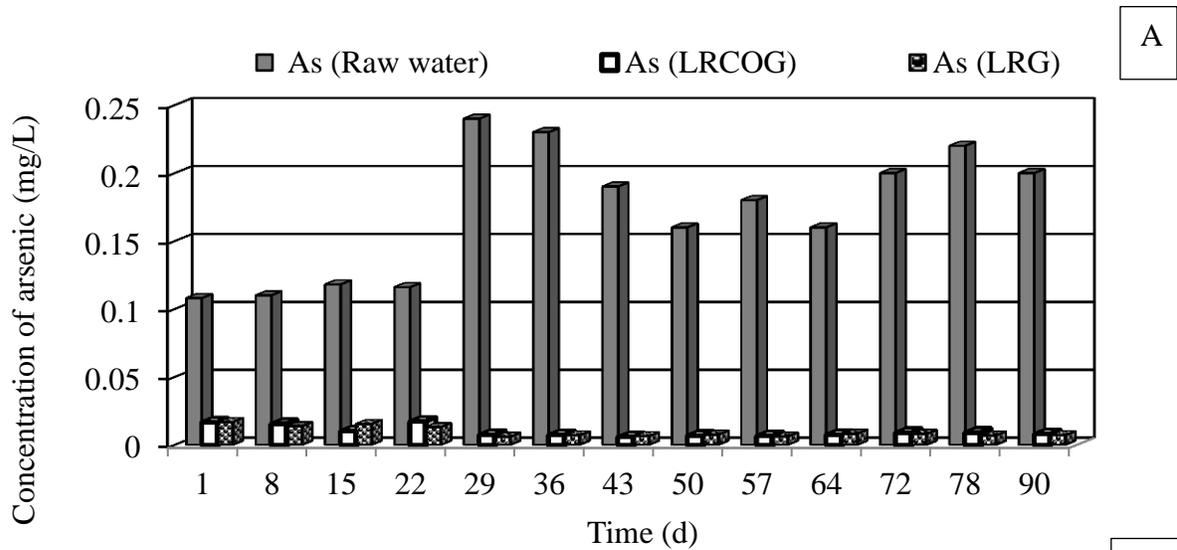
Figure 2: Variation of pH of the raw water of well and the effluents collected at the outlet of LRCOG and LRG

3.1.2. As, Ni and Pb removal

The concentrations of As increased slightly from an initial value of 0.10 to a maximum of 0.24 mg/L in the raw water (Fig. 3A). But this concentrations were significantly highest than effluents of LRCOG (0.0057 to 0.017 mg/L) and LRG (0.0058 to 0.016 mg/L). There are no significant differences in As concentrations between the two reactor (test t: $p > 0$).

The concentrations of Ni in the two reactors were significantly lower than those of the raw water (Fig.3B). The concentrations of Ni were between 0.14 and 0.25 mg/L in the raw water, 0.0008 and 0.0017 mg/L in LRCOG, 0.0009 and 0.0019 mg/L in LRG.

Concentrations of Pb measured in influent and effluent during 90 days experimental period are given in Fig.3C. Effluent concentrations of Pb in LRCOG (0.01 to 0.015 mg/L) and LRG (0.001 to 0.014 mg/L) were below influent concentration of Pb (0.06 to 0.12 mg/L).



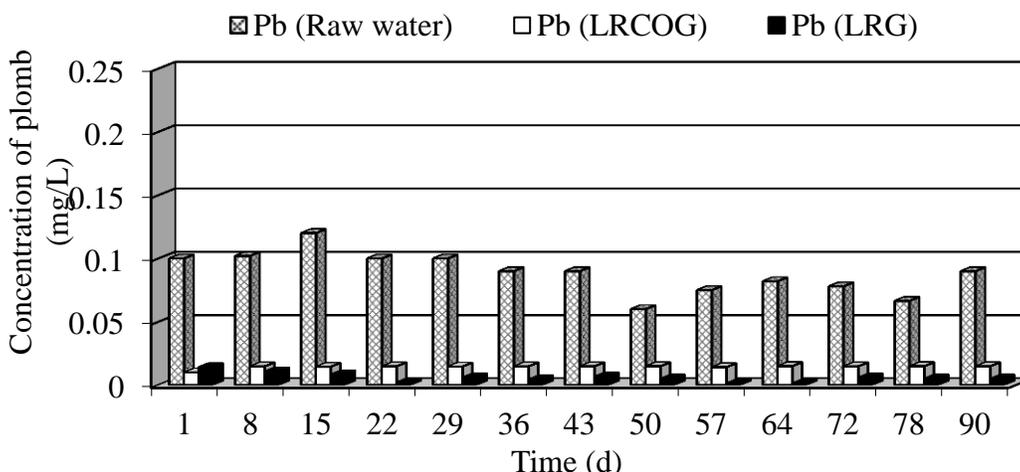


Figure 3: Concentrations of arsenic (A), nickel (B) and lead (Pb) of the raw water and Effluents collected at the outlet of LRCOG and LRG

3.1.3. Removal Efficiencies

The comparison among the removal efficiencies of reactor media indicates that LRG were relatively higher than LRCOG (Fig. 4). Indeed, As, Ni and Pb removal for LRG were $98.63\% \pm 0.39$, $99.73\% \pm 0.15\%$ and $97.94\% \pm 0.55$ respectively. The removal percentages in LRCOG were $98.33\% \pm 0.41$, $99.17\% \pm 0.20$ and $96.09\% \pm 1.04\%$ for As, Ni and Pb respectively.

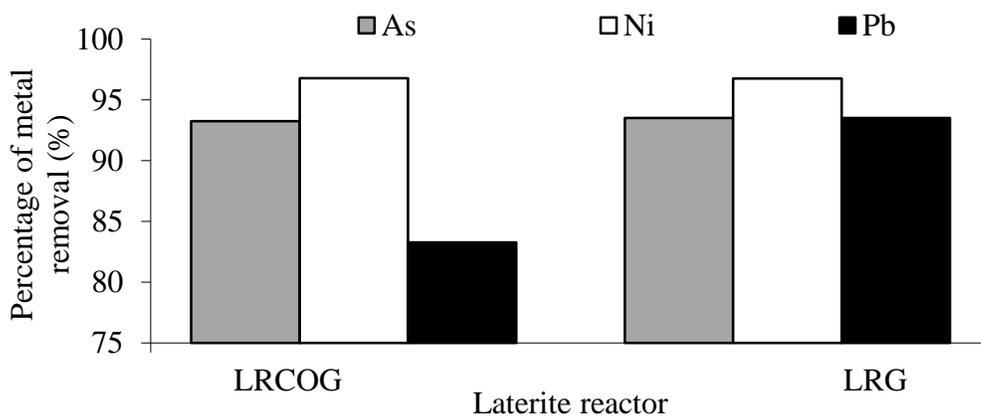


Figure 4: Removal efficiencies percentage of laterite material

3.2. Discussion

The highest effluent pH value could be attributed to the neutralization of H^+ of well water and basic character of laterite. Concerning the neutralization of H^+ , De Haas, Wentzel and Ekama (2001) reported that H^+ were adsorbed by the oxides of laterite, increasing the alkalinity. As to the basic character of laterite, Godfrin and bladel (1990) and Tessier, Campbell and Carignam (1990) found that the precipitation of the hydroxides or oxides in the laterite increase the pH of two reactors. pH of effluent was acceptable according to WHO standards.

After treatment of contaminated water, the concentrations of the different heavy metals in effluents of the two reactors respected the WHO drinking water guide and were significantly lower than those of the raw water. This result is attributable to the sesquioxides laterites which possess OH groups capable of ionizing in an aqueous medium. This reaction produces stable compounds which are trapped in the filter bed. Indeed, the laterite which was highly microporous (Lawane, Pantet, Vinaïand Thomassin,2011; Coulibaly, 2014) allow themselves to cross by water which will separate the iron hydroxides in solution in Fe^{2+} and Fe^{3+} . These ions will form complexes with each heavy metal (Rancourt, 1993; Sorgho, Paré, Guel, Zerbo, Traoré and Persson, 2011). The decrease of concentrations of heavy metal in the effluents was also explained by the pH (Bataillard, Guérin, Lions, Girondelot, Laboudigue, Van der Lee, Raepsaet and Gallien, 2010; Ziati, Hazourli, Nouacer, Khelaifia and Merzoug, 2013; Coulibaly, 2014). Indeed, pH influences the distribution of shapes of the heavy metal present in the raw water and actived adsorption sites of the laterite. For pH below 6, the hydroxyl groups at the periphery of oxides on the laterite are protonated and acquire a positive charge. These sites are then available to react and adsorb As. At pH greater than 6, the surface of the laterite is negative, so the Pb^{2+} and Ni^{2+} will adsorb on the sites of the surface.

Arsenic, nickel and lead removal percentages were higher for LRG than reactor LRCOG. This difference percentage is caused by the size of grains of the laterite. LRG is filled with granules of laterite whose size is smaller than the coarse laterite LRCOG, offering so a greater surface of contact (Kannan and Sundaram, 2001; Pavel, Pavel and Lukás, 2007). This increases the retention capacity of the heavy metals in LRG. The percentages of removal of heavy metal were higher than the size of the laterite. This high retention could be explained by the specific surface that is particularly important than the laterite height is high (40 cm) in the two reactors (Sedira, 2013). In addition, the meso and micropores that have mineral structures laterite are areas of high interaction energies; which favor the adsorption of large quantities of heavy metal).

Regarding the percentages of As removal, the results were in agreement with those of Maji, Pal and Pal (2006). Indeed, these authors in their investigation on the characteristics of the adsorption of arsenic in the soil lateritic collected in the zone Gopali India observed that the laterite could eliminate up to 98% of arsenic.

For the Pb, the percentages of reduction (96%) obtained by Sorgho, Paré, Guel, Zerbo, Traoré and Persson(2011)were similar of our two reactors.

The removal percentage of Ni in this study were relatively higher than those of Manceau, Charlet, Boisset, Didier and Spadini (1992) (55 to 89%) and Quantin, Becquer and Berthelin (2002) (85%). This difference could be explained by the quantity of iron available in the oxides. Indeed, these authors have used a mixture of sand and metal oxides as solid whose quantity of iron is 30.45% which is lower than 45.10% of iron contain in the laterite of this study.

The adsorption of heavy metal on the two types of laterite particle size was in the same order of effectiveness ($Ni > As > Pb$). This sequence of adsorption preferential of nickel could be interpreted by the value of radius of van der Waals. Indeed, the radius of van der Waals of Ni is smaller than those of As and Pb; thereby, the inserting of Ni is faster, so the Ni will be better adsorbed (Chouchane, 2009).

4. Conclusion

Metal contamination of groundwater is a real phenomenon and should not be neglected because it record of the concentrations exceeding the values guideline set by WHO. This contamination is anthropogenic. Laterite coarse grain and granule size have been used as adsorbents for As , Ni and Pb. the acidic pH in raw water become neutral and stretches towards the basicity after treatment in the two reactors . Concentrations of As (0.10 to 0.24 mg/L), Ni (0.14 to 0.25 mg/L) and Pb (0.06 to 0.1 mg/L) in raw water are higher than WHO guidelines. This study showed an increase satisfactory of the removal percentage of these heavy metals. The results obtained showed a capacity of adsorption of the coarse laterite of the order of $98.3 \pm 0.4\%$, $99.2 \pm 0.2\%$ and $96.1 \pm 1.1\%$ respectively for As, Ni and Pb. With the laterite in form of granules, the capacities of adsorption obtained were of $98.6 \pm 0.3\%$ for As that of the Ni is of $99.7 \pm 0.2\%$ and $97.9 \pm 0.5 \%$ for Pb. At the end of this work, the results showed that the technical of adsorption with the laterite have a better elimination of heavy metal.

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