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Attenuation of the proportion of humic acid in the landfill leachate by laterite

Yoh COULIBALY[1]*, Tiangoua KONE[1], Pétémanagnan Jean-Marie OUATTARA[1], Sandotin Lassina COULIBALY[2], Jean Aimé MBEY[3]**

[1]Department of Environmental Sciences and Management, University of Nangui Abrogoua, 01 BP 801 Abidjan 01, Abidjan, Côte d'Ivoire
[2]Department of Environnent and Sustainable Development, University of Man, BP 40 Man, Côte d'Ivoire
[3]Department of Inorganic Chemistry, University of Yaoundé I, Cameroon
**Corresponding author, Email address: coulibalyyoh@gmail.com*
***Corresponding author, Email address: tiangoua.kone@yahoo.fr*

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coulibalyyoh@gmail.com
Phone: +225 0707123425

Abstract

To limit environmental pollution due to humic substances from household refuse dumps in Developing countries (DCs), a treatment by adsorption through laterite in a batch test has been explored. The study consisted of characterizing the laterite before the start of treatment. Mineralogical characterization of laterite carried out by XRD and infrared revealed the presence of oxides and oxyhydroxides, which are an asset for treating humic substances in leachate. Industrial humic acid was used as a model pollutant to study adsorption on shale and laterite through batch adsorption tests. The results showed that the optimal dose and the equilibrium time followed are 80 g/L and 90 minutes with the laterite. High degradation rates were obtained at pH 3.5 and 4.5 with the laterite. The optimum concentration was 100 mg/L. The Kinetic study showed that the pseudo-second order model better-fitted sorption data for humic acid onto laterite. Furthermore, sorption happened with an intraparticle diffusion model, underlining contribution from active sites inside the pores. Langmuir and Freundlich models better fitted experimental data for sorption isotherms.

1. Introduction

The brown coloration, characteristic of the presence of dissolved organic matter in natural waters, can be accentuated by the input of organic matter from anthropogenic wastewater such as landfill leachate [1]. It should be noted that humic substances, in general, are naturally present in surface waters with a content of between 1 to 15 mg $C.L^{-1}$. However, due to its high organic compounds content, leachate has been identified as a potential source of groundwater and surfaces water pollution [2]. This leachate may contain high levels of organic matter, consisting mainly of humic substances refractory to biodegradation, ammoniacal nitrogen, heavy metals, organochlorines, and inorganic salts, in comparison to WHO (World Health Organization) discharge standards [3,4].

As a prelude to the previous, photosynthetic activity may be limited in the surface layers of surface waters [5]. In fact, humic and fulvic acids in leachate, consisting of large amounts of high molecular weight components, such as phenolic and aromatic compounds, are mainly responsible for the brown color and odors of water [4]. They constitute an average of 30 to 50 % of dissolved organic carbon and sometimes 90 % in some very colored waters [4]. Vigneault [1] studies on dissolved humic substance interactions with unicellular algae have shown that humic substances are a source of carbon, nitrogen, and phosphorus in natural waters. According to the author, humic substances could also promote the bioavailability of metals in natural waters. The accumulation of these compounds in water will promote the enrichment of the aquatic environment in nutrient salt, hence the phenomenon of eutrophication. Also, humic substances are currently a concern for drinking water treatment plants.

Indeed, the presence of organic compounds dissolved in surface water at a high content increases the cost of treatment for drinking water production. Then, they can pose other problems such as the deterioration of the organoleptic quality, the bacterial development in the pipes of the distribution network, and subsequently, the aggravation of corrosion [7,8,6,9]. Finally, significant chlorine consumption during disinfection can also lead to chlorinated by-products potentially toxic to humans, mainly trihalomethanes and haloacetic acids [10,8].

There are many treatment processes developed to remove humic substances from water. We can cite physicochemical processes such as sorption, coagulation-flocculation, chemical precipitation, reverse osmosis, etc. [11,12,13,14,15,16]. However, the prohibitive costs of some of these techniques make them inapplicable in the context of developing countries such as Côte d'Ivoire.

The sorption treatment of humic substances on mineral surfaces has shown its effectiveness, according to some authors, either on natural adsorbents or on synthetic adsorbents [17,18,19]. They can be in granules, powder, extrudates, or fabric [20,21]. To find low-cost efficient easy implementable processes using natural adsorbents, the study used geo-materials such as laterites which are endogenous materials abundant in nature, to reduce humic acid in leachate. Indeed, the study by Coulibaly [22] has shown that laterite from Côte d'Ivoire is an effective adsorbent for the retention of phosphates in domestic wastewater. Koua-Koffi [23] study on arsenic sorption onto laterite effectiveness. The study by Ama [24] on the treatment of domestic wastewater by an intermittent filter lined with laterite showed the best pollutant removal efficiency. In fact, laterites have a high proportion of iron hydroxide and aluminum oxide [22]. The sorption of organic matter onto the surface of these minerals can be governed by ligand exchanges, hydrophobic interactions, electrostatic interactions, or the formation of hydrogen bonds [25,26,27,28]. Therefore, the treatment or fractionation of these compounds will make it possible to preserve aquatic environments. In this context, this study aims to investigate a treatment by sorption of humic acid from leachate on laterites.

For this purpose, an industrial humic acid molecule was chosen as a model pollutant for this study. Thus, to achieve this objective, the study specifically consists of (i) characterizing the laterites before the sorption tests, (ii) studying the reduction of humic acid by the laterite through adsorption tests in batch, and (iii) modeling the kinetics and the sorption isotherms.

2. Methodology

2.1 Sourcing and preparation of laterite and Chemicals

2.1.1. Sourcing and preparation of laterite

The mineral surface used to carry out this study is laterite, it was taken at Sinématialy (9 ° 35 '' N and 5 ° 23 'W) in the North of Côte d'Ivoire according to the geological map of the Côte d'Ivoire adapted by Tagini [29] and modified from Ouattara [30]. The laterite blocks collected were washed and steamed, then crushed with a hammer (**Figure 1**). The powders obtained using a mill were sieved using a Saulas sieve (NF.X 11.501) at 250 µm. The chemical properties of the ground material were analyzed by X-ray Diffraction (XRD) and Infrared. A Bruker D8 Advance Diffractometer operating on a copper anode was used to identify the mineralogical phases of the laterite. A Brukers brand Alpha-p spectrometer, an instrument equipped with a KBr beam splitter and a TCD detector, was used to characterize the laterite.

Laterite block

Laterite crushed < 250 µm

Figure 1: Blocks and crushed laterite

2.1.2. Sourcing of Chemicals and Humic acid solution preparation

Industrial humic acid, sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich® (AH) in France.

The industrial humic acid taken as a model pollutant to carry out this study had already been characterized by Coulibaly [4]. They showed similarities between synthetic humic acid and extracted humic acid from the Akouédo landfill leachate.

Humic acid solutions were prepared with distilled water (conductivity 6 - 7.6 µS/cm and pH = 6.3). In fact, a 1000 mg/L humic acid stock solution was prepared by adding 1g humic acid salt to one liter of distilled water with stirring. Successive dilutions obtained standards used for the analysis until the desired concentrations of humic acid. The concentrations were indirectly determined through OD measurements, and a calibration process was carried out from stallions. Calibration lines were performed at wavelength ≥ 286 nm using a DR 6000 UV-Visible Spectrometer.

2.2 Experiments

2.2.1. Characterization of the laterite

X-ray diffraction (XRD) data were obtained by reflection on a powder material by Bruker D8 Advance Diffractometer. To this end, the analysis involves subjecting 1 g of powdered laterite installed in a capsule to a monochromatic X-ray beam and collecting the diffraction spectrum it emits. Thus, X-ray Diffraction (XRD) analyzes were performed on the Bruker D8 Advance spectrometer, operating on a copper anode at the University of Liège. The detection threshold of an ordered mineral species is around 1 to 2 %. The assignment of peaks to the corresponding minerals is done by comparing them with the data provided by the American Society for Testing and Materials (ASTM) files [31].

IR analysis of the laterite was carried out using a Brukers brand Alpha-p IR spectrometer equipped with a KBr beam splitter and a TCD detector at the Inorganic Chemistry Laboratory. Applied from the University of Yaoundé I. Thus, the measurements were carried out in diffuse reflection with a mass of 2 mg of laterite sample powder obtained using a mill and sieved with a Saulas sieve (NF. X 11.501) with a particle size of less than 250 µm (Figure 1). This ground material obtained from laterite is mixed with 300 mg of potassium bromide to reduce energy losses. This mixture is pressed in the form of a pellet in a die. Radiation penetrates inside the sample, undergoes reflection, refraction, diffusion, and absorption effects, and is then re-emitted in all directions of a hemispherical space. The absorption spectra were also carried out in absorbance mode for a wave number scan which varies between 4000 and 400 cm^{-1} [32]. They make it possible to reveal the presence of specific atomic groups in a given phase.

2.2.2. Optimization of humic acid sorption parameters

The experiments were carried out in a non-renewed medium (batch test) in 200 ml Erlenmeyer flasks at 26 °C ± 0.3 and stirred using a magnetic stirring set at 300 rpm. A 15 mg/L solution was prepared from the stock humic acid solution to run the test. Laterite sorption process factors, including adsorbent material mass, stirring time, reaction medium pH, and adsorbate concentration, were determined.

Mass optimization consisted of varying it in steps of 0.1 g and mixed with 50 ml of the humic acid solution. The solutions were stirred before centrifugation at 4000 rpm for 15 min after the stirring time. The UV-Visible Spectrometer analyzed the filtrates obtained to follow the reduction of humic acid in solution. The ratio $[AH]/[AH]_0$ and the abatement rate were calculated, according to equation (1).

$$R[\%] = \frac{C_0 - C_t}{C_0} * 100 \qquad (\boldsymbol{Eqn.1})$$

With: C_0 (mg/L) the initial concentration of humic acid and Ct (mg/L) the equilibrium concentration.

Regarding laterite masses, the stirring time varied in steps of 10 min for 1h followed by 60 min steps until saturating the materials. The residual humic acid concentrations were determined at each time step. This was performed as $[AH]/[AH]_0$ ratios for each time, and the abatement rate was calculated according to the equation (1) above.

The influence of the reaction medium pH on humic acid sorption onto the laterite was determined at different pH (3.5; 4.5; 6.5; 8.5 and 9.5) in the same reaction conditions as before. The pH value was adjusted using 0.1 M hydrochloric acid solution or 0.1 M sodium hydroxide solution. Residual humic acid concentrations were determined at the equilibrium, and the ratio $[AH]/[AH]_0$ and the abatement rate were calculated according to equation (1) above.

2.2.3. Kinetics and the influence of initial humic acid concentrations

Sorption kinetics for synthetic humic acid onto laterite provided information on the binding rate of humic acid molecules onto the solid mass and the adsorption capacities at the equilibrium of the adsorbent with respect to -vis of humic acids, are followed. During these kinetic tests, humic acid concentrations were set up at 20, 40, 80, and 100 mg/L for a reactant medium pH value of 6-6.7. This was performed at the optimum mass and stirring duration values as determined under the same reaction conditions described above. These experiments enabled us to determine the laterite's adsorption capacity (Qt). The residual concentrations of humic acid in solution were measured at each time point (t) (Ct). The humic acid concentration per mass unit of laterite at the time (t) was calculated according to equation (2):

$$q_t = \frac{(C_0 - C_t) \times V}{m} \qquad (\boldsymbol{Eqn.2})$$

With qt (mg/g) the adsorption capacity after a stirring time t, Ct the humic acid concentration at time t (mg / L), Co the initial humic acid concentration (mg / L), m the mass of the adsorbent (g) and V the volume of the solution in L.

2.2.5 / Sorption isotherm

Adsorbent masses corresponding to the optimal masses of laterite were added to humic acid solutions previously prepared at initial concentrations ranging from 15 to 100 mg/L, to perform a sorption isotherm. The whole humic acid solution containing laterite was stirred at 300 rpm until reaching equilibrium time at 26.3 °C and pH 6 - 6.7.

The supernatant was collected, and the humic acid concentrations were determined. The quantity of organic matter fixed per mass unit (Qe in mg/g) at various equilibrium times was calculated according to the equation (3):

$$\mathrm{qe} = \frac{(\mathrm{C_{0-}C_e}) \times \mathrm{V}}{\mathrm{m}} \qquad \textbf{(Eqn. 3)}$$

Where: qe (mg / g), the adsorption capacity at equilibrium; Ce, the equilibrium humic acid concentration (mg / L); Co, the initial concentration of humic acid (mg / L); m, the mass of the adsorbent (g); and V, the volume of the solution (L).

2.2.5. Modeling sorption kinetics

Among the adsorption models developed, three kinetic models were used in this study, including two of the reaction models (pseudo-first order and pseudo-second order) [33,34]. and one diffusional model (intra-particle diffusion of Weber and Morris [35]) [36]. Kinetic equations and their linearized forms of the models are presented according to equations 4, 5, 6, and 7.

- ✓ **Pseudo-first order: *qe*, k$_1$**

$$\mathrm{Log(qe - qt) = Log(qe)} - \left(\frac{\mathrm{k_1}}{2{,}303} * \mathrm{t}\right) \qquad \textbf{(Eqn. 4)}$$

Where: qe and qt, the amount of solute adsorbed respectively at equilibrium and at time t (mg/g); k$_1$, the adsorption rate constant (min^{-1}).

The amount of solute adsorbed at equilibrium qe and the pseudo first order rate constant k$_1$ are determined from the graphical representation of Log (qe-qt) as a function of time t.

- ✓ **Pseudo-second order: qe, k$_2$**

$$\frac{\mathrm{t}}{\mathrm{qt}} = \frac{1}{\mathrm{k_2\,q_e}^2} + \frac{\mathrm{t}}{\mathrm{Q_e}} \qquad \textbf{(Eqn. 5)}$$

$$\mathrm{h = k_2 q_e}^2 \qquad \textbf{(Eqn. 6)}$$

Where: k$_2$, the speed coefficient (g.mg-1min-1); h, initial rate of adsorption.

Plotting 1/qt as a function of time t gives a linear curve with a slope of 1/qe and a y-intercept of $1/k_2qe^2$.

- ✓ **Diffusion adsorption model : Intra-particule scattering k$_d$, C**

$$\mathrm{q(t) = k_d t^{1/2} + C} \qquad \textbf{(Eqn. 7)}$$

Where: k$_d$ mg / (g.h$^{1/2}$): the intra-particle diffusion constant, C (mg / g): constant representative of the thickness, k$_d$ depends on the diffusion coefficient of the species considered as well as on the size and number of pores borrowed within the adsorbent material.

2.2.6. Modeling of isotherms

The Langmuir and Freundlich models were used in this study. Their mathematical expressions are given by equations 8 and 9.

- ✓ **Langmuir isotherm (1918)** :

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m k_L} * \frac{1}{C_e}\right) \qquad \textbf{(Eqn. 8)}$$

Where: q_e is the adsorbed quantity of the solute at equilibrium (mg / g), Ce, the concentration of the solute at equilibrium (mg / L), q_m (mg / g) represents the maximum adsorption capacity, and k_L the Langmuir affinity constant.

- ✓ **Isotherm by Freundlich (1906)** :

$$q_e = k_f * C_e^{1/n_f} \qquad \textbf{(Eqn. 9)}$$

Where: q_e, amount adsorbed at equilibrium per gram of solid (mg / g); Ce, adsorbate concentration at adsorption equilibrium (mg / L); k_f and $n_f > 1$ Freundlich constants characteristic of the efficiency of a given adsorbent with respect to a given solute. Thus, the higher the k_f value, the greater the adsorption.

3. Results and Discussion

3.1 Characteristic of laterite

The analysis results made on the crushed laterite by X-ray diffraction (XRD) are presented in **figure 2**. These results show that the laterite would contain several minerals including a single clay mineral which is kaolinite ($Si_2O_5Al_2(OH)4$ (7.18; 4.37; 3.55; 2.51 and 1.82 Å). The main crystalline forms of iron oxides and oxyhydroxides are hematite (Fe_2O_3) (2.71; 2.51 and 20.20 Å), goethite (FeO (OH)) (4.17 Å), maghemite (Fe_2O_3) (1.98 Å); aluminum hydroxides revealed the presence of gibbsite (Al (OH)3, (4.86; 4.37; 3.18; 2.45, and 2.39 Å), finally the presence of calcite ($CaCO_3$) (3.04; 2.51 and 2.27 Å) and quartz (SiO2)(4.27; 4.25; 3.34; 2.45; 2.28; 2.13 and 1.67 Å) were confirmed. The assignment of these peaks to the corresponding minerals was made by comparing them with data provided by the American Society for Testing and Materials (ASTM) files [31].

Infrared analysis (FTIR), as a mineralogical analysis tool and complementary to X-ray diffraction, detected the presence of the same minerals as that of XRD in the laterite. Thus, the spectrum of the FTIR analysis of laterite is shown in **Figure 3** [37,38,39]. Their genesis could explain the abundance of these minerals in laterite. In fact, the laterite from Côte d'Ivoire is assumed to be produced from the weathering of granite and phyllites or from the hydrolysis of carbonate or silicate rocks [40,22]. This is why we distinguish between hydrates of alumina and iron, which gives the characteristic red color of laterites.

The mineralogical nature of the laterite revealed by its results would be an asset for carrying out treatment tests by adsorption of humic substances from the leachate [26,41].

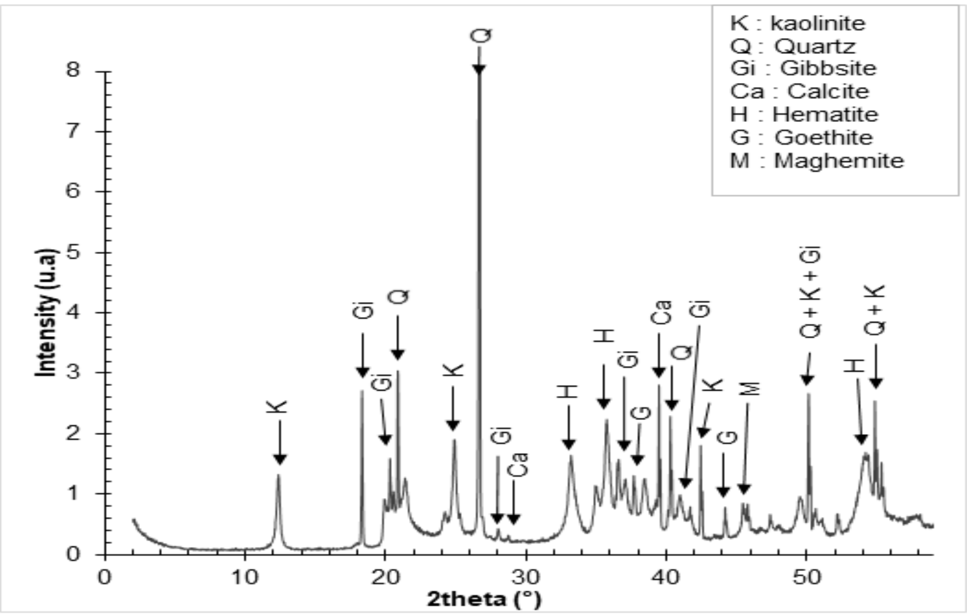

Figure 2: XRD spectra of laterite.

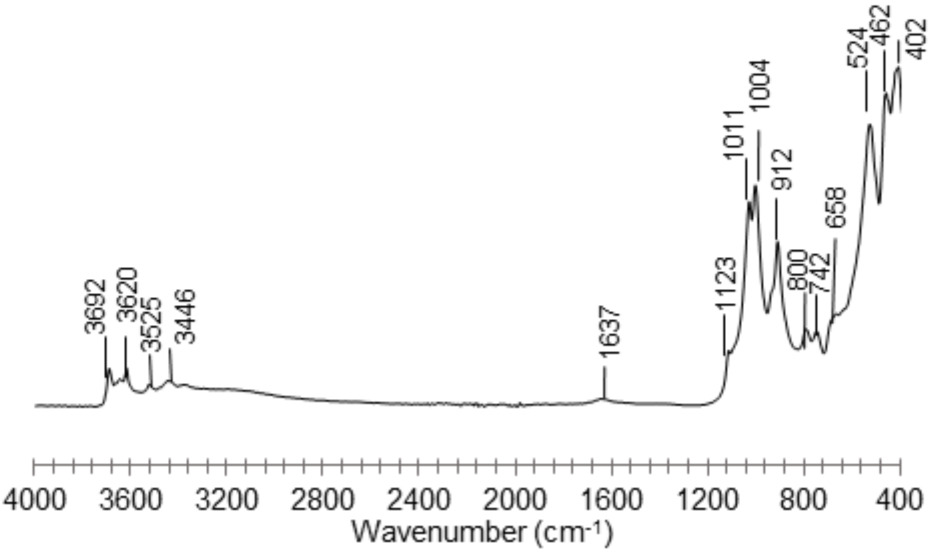

Figure 3: Infrared spectrum of raw laterite ground material between 4000 to 400 cm^{-1}.

3.2. Optimum parameters for adsorption of humic acid on laterite

3.2.1. Optimal mass of laterite

Figure 4 plots humic acid abatement rates as a function of laterite masses. Indeed, it is observed that the curve has three (3) phases, including a rapid one characterized by a strong positive slope, a second slowing phase characterized by a weak positive slope, and a slow regression phase characterized by a weak negative slope. We note that increasing adsorbent masses in the reaction medium inversely influences the reduction rate. Therefore, the optimum concentration is 80 g/L for laterite with a yield of 93.50 %. The adsorption of HAs in the first phase could be explained by the fact that sorption surfaces of the materials are prominent in this phase. The slowdown observed in the second phase is justified by the low availability of the sorption surface. Regressions observed at high concentrations of materials could be due to materials deposit leading to aggregation. Thus, from a given concentration of materials (optimal concentration), any supplementary addition of materials does not contribute to adsorption [41].

Large amounts of mineral compounds on the surface of materials such as iron, aluminum, calcium, and magnesium could justify the significant organic matter retention from the humic acid type. Indeed, organic particles essentially associate with mineral particles through electrostatic bonds made possible by hydroxide radicals to form aggregates [27]. This could result from several types of functional surfaces present within mineral particles, such as surfaces presenting hydroxylic groups, deriving from iron and aluminum, which gives several possibilities of bonds with organic matter [26]. According to Khansaa [41], the addition of inorganic salt can also influence the adsorption reaction by affecting the molecular structure of HA. This result could be attributed to the coordination surface of HA in ambient suspensions of mineral particles [42,25,43]. Similar trends have been observed by Coulibaly [44] during the adsorption of phosphates to laterites. Guergazi [45] corroborate these results. They have shown that the removal of humic substances varies with the mass of adsorbent involved indeed.

Ouakouak's [46] study regarding the sorption of a synthetic solution of humic substances by activated carbon goes against the results of the present study, as he observes an increase in the elimination efficiency of the organic matter when the mass of adsorbent introduced increases.

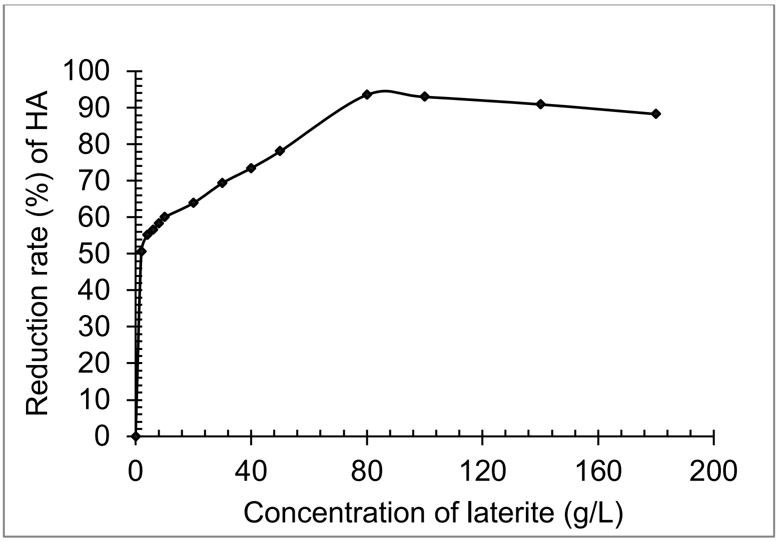

Figure 4: Curve of the optimal laterite concentration.

Experimental conditions: initial concentration of humic acid = 15 mg/L; Stirring speed = 300 rpm, stirring time = 24 hours; pH = 6.5; Temperature = 26 °C ± 0.3, the mass of ground laterite between 0.1 and 12 g.

3.2.2. Optimal stirring time

The evolution of humic acid sorption onto the laterite as a function of the stirring time is shown in **Figure 5**. We note that the influence of the stirring time on humic acid sorption onto the laterite shows two phases. Equilibria are reached after 90 min on the laterite with adsorption maxima of 96 %. These relatively short contact times demonstrate the rapidity of the phenomenon. This could be due to the complexation between the functional groups of humic acid and the oxides present on the mineral surfaces of the two adsorbents. Most of the works on the sorption kinetics of organic pollutants in soils show that the adsorption was a rapid phenomenon where often more than 50 % of the solute is adsorbed in a few minutes [47,48]. According to Calvet [49], a few hours of contact are generally sufficient to achieve equilibrium. Kleber [50] have also shown that natural organic matter has similar functional groups, mainly carboxyl, and alcoholic/phenolic OH groups, which therefore react with surface minerals. On the contrary, the study conducted by Koua-Koffi [23] on the arsenic sorption onto laterite, sandstone, and shale showed that the time required to reach equilibrium is 3, 5, and 8 hours of agitation, respectively for sandstone, laterite and slate shale.

Also, according to Blacke [51], sorption of organic compounds such as humic substances could depend on their affinity to the adsorbent and interactions with the solvent itself.

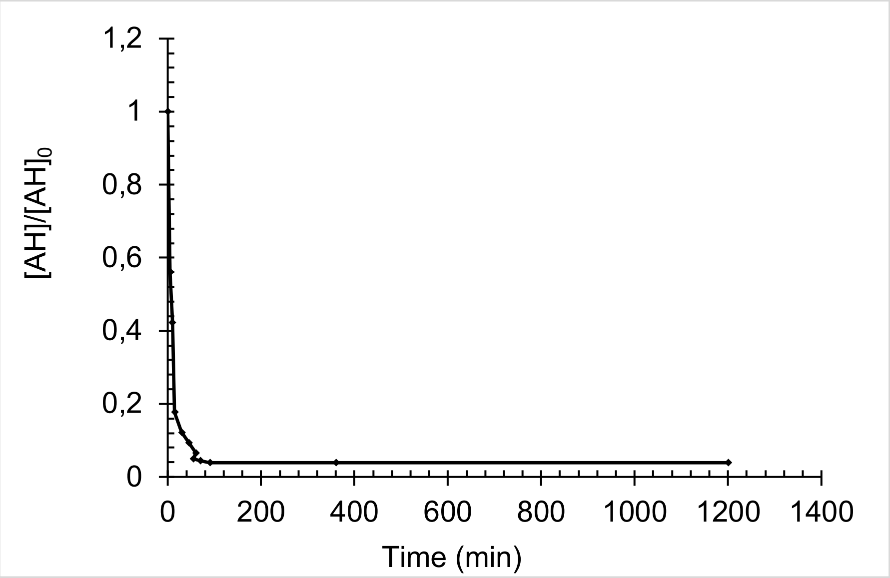

Figure 5: Degradation of humic acids as a function of the stirring time on the laterite.
Experimental conditions: initial concentration of humic acid = 15 mg / L; Stirring speed = 300 rpm; stirring time = 24 hours; pH = 6.5; Temperature = 26 ° C ± 0.3.

3.2.3. Influence of pH on the adsorption of humic acid

Figure 6 plots $[AH]/[AH]_0$ ratios for humic acids sorption onto laterite as a function of the pH of the medium. In general, the curve shows that changes in adsorbed humic acids masses are inversely proportional to pH increases. Sorption is quite high at pH values between 3.5 and 5.5.

This change in laterite could be justified by modifying the surface charges of materials for each pH value for the medium changes. Indeed, in an acidic medium, the surface charge of laterites is positive until reaching the point of zero charge or the isoelectric potential (ZPC) of (oxy)hydroxide surfaces is 6.1 [22]. For pH greater than 6.1, the surface charges are negative. Thus, in an acidic medium, the carboxyl functional groups of humic acids are mainly adsorbed on the protonated surface of the hydroxyl groups of the laterite and as the pH increases the reaction takes place with the phenolic groups of humic acids [42,52].

Indeed, low pH values would be favorable to the formation of strong surface complexes of the internal sphere, while at neutral and alkaline pH, complexation of the relatively weak external sphere would dominate [53,54,55,56,57].

Humic acid contains a wide range of functional groups (COOH, OH, NH_2, etc.). According to Daifullah [58], more of these groups are in an uncharged state, hence more adsorbable at lower pH. Therefore, a less hydrophilic part of the humic polymer would bind to hydrophobic compounds, and the binding constant would increase as the pH is reduced. Wang [52] showed that electrostatic interactions are more critical when the pH decreases among the adsorption mechanisms. Hydrophobic interactions could also occur during the adsorption of AH [59]. The results obtained from several authors who have achieved sorption of humic substances on clays, red blood cells, and alumina are inversely proportional to the pH [60,61,62,63]. The adsorption of HA on bentonite was found to be inversely proportional to the increase in pH due to the increased repulsion between HA and bentonite [64].

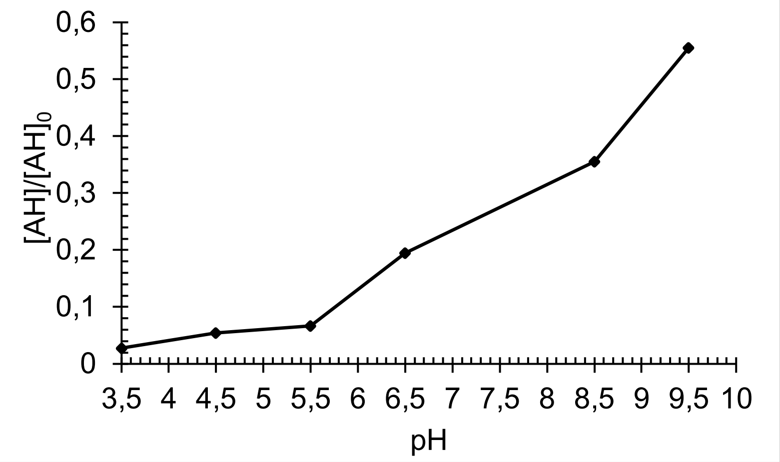

Figure 6: Effect of pH on humic acids removal by laterite.
Experimental conditions: initial concentration of humic acid = 15 mg/L; Stirring speed = 300 rpm; pH = 3.5; 4.5; 5.5; 6.5; 8.5; 9.5; Temperature = 26 ° C ± 0.3.

3.2.4. Influence of initial concentration on humic acid retention kinetics

Figure 7 presents sorption capacities (Qt) corresponding to each material as a function of time. These capacities evolve with increasing HA concentration.

Results also show that HA sorption efficiency increases with an increasing initial concentration of HA in solution (20, 40, 80, 100 mg/L). This could be explained by the fact that an increase in HA concentration offers more binding sites on the carboxylic groups.

Therefore, electrostatic attraction phenomena could occur between the functional groups of humic acids and certain charged active sites of laterite and shale. This is due to the shift in equilibrium in the direction of binding of HA molecules [65]. According to Weng [66], the evolution of adsorption of organic matter would vary with ionic strength and ligand types. Thus, increasing ionic strength was favorable for HA sorption onto goethite. This could be attributed to a decrease in molecular size and stronger competition with the ions in the electrolytes for surface charge neutralization. According to Kleber [50], sorption of organic ligands onto mineral surfaces would depend upon their concentration in the solution and the solution composition. The low concentrations allow organic polyelectrolytes to establish a maximum of strong inner sphere surface complexes on surface oxides [67].

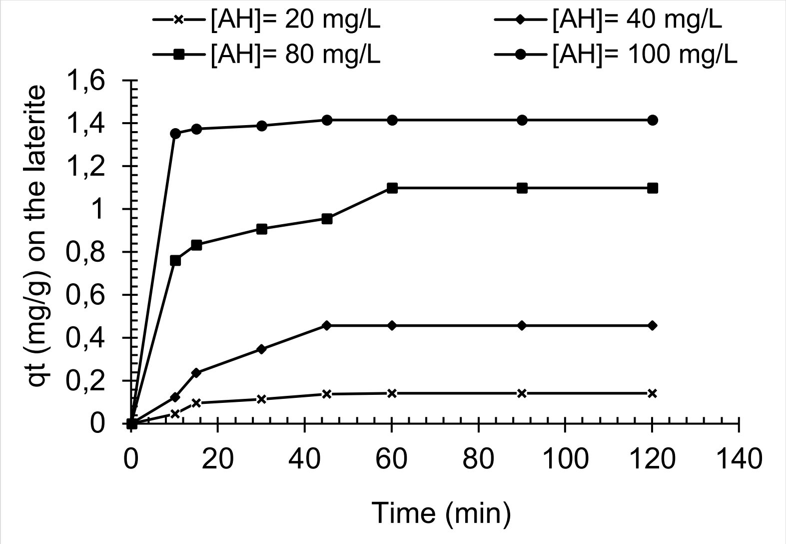

Figure 7: Retention capacity as a function of time on the laterite.

3.3. Kinetic modeling

3.3.1. Pseudo-first order model

Figure 9 and **Table I** show results for applying the pseudo-first order kinetic model to fit humic acid sorption experimental data at different concentrations on laterite. We note that whatever the concentrations of humic acid, the humic acid sorption capacities determined by a series of tests on the laterite (Qe, exp, mg/g) are different from those calculated theoretically (Qe.cal, mg/g). However, correlation values (R) vary between 0.60 and 0.80 for laterite regardless of concentrations. These low values show that a first-order law cannot describe the adsorption of humic acids to these materials.

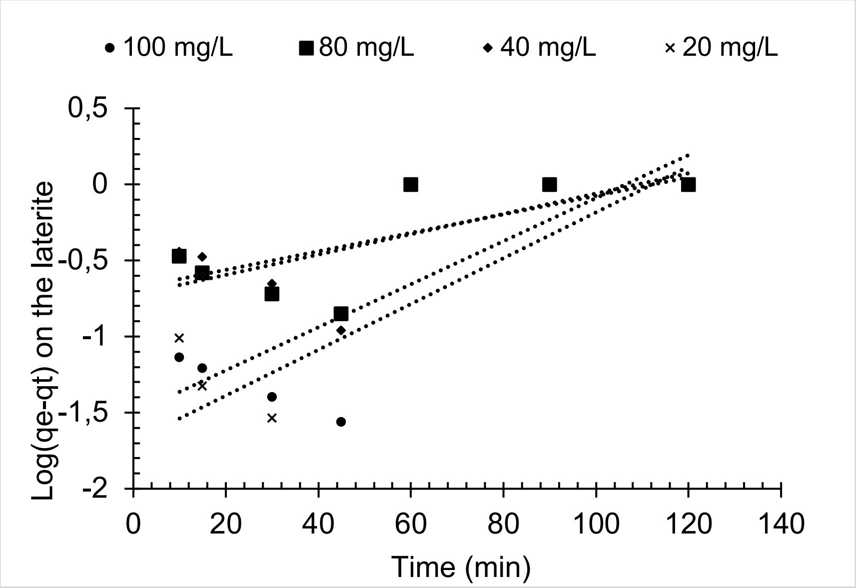

Figure 9: Pseudo-first order linearization for HA adsorption to laterite.

Table I: Kinetic parameters relating to the pseudo-first order model.

Parameters / **Massive**	**C_i (mg/l)**	**$Q_{e,exp}$ (mg/g)**	**$Q_{e,cal}$ (mg/g)**	**k_1 (min^{-1})**	**R**
Laterite	20	0.10	0.60	$4.50\ 10^{-3}$	0.70
	40	0.50	1.20	$8.10\ 10^{-3}$	0.65
	80	1.10	1.80	$15.40\ 10^{-3}$	0.70
	100	1.40	1.90	$22\ 10^{-3}$	0.80

3.3.2. Pseudo-second order model

Figure 10 shows the results of applying the pseudo-second order kinetic model to the experimental data from the adsorption of humic acid by laterite. Furthermore, the results of various indices inherent in the model are listed in **Table II**. We note that whatever the humic acid concentrations of 20, 40, 80, and 100 mg/L, there is a good correlation between the experimental adsorption capacities (qe.exp) and the theoretical values (qe.cal) for laterite.

Also, correlation coefficient values vary around 1, which thus shows the conformity of the theoretical data with those obtained during the batch tests. The pseudo-second order model would better describe the adsorption of humic acid to laterite. The results showed that the pseudo-second order model better simulates the experimental data. This suggests that chemosorption may be the dominant mechanism in the adsorption of humic acid to shale and laterite [68,69,70,71]. Koua-Koffi [23] and Kpannieu [72] came to similar findings regarding sorption on laterite and shale. The results of Abdel-Rahman [71] showed that sorption of AH onto smectite followed the pseudo-second order pattern under various conditions. In fact, chemisorption takes place through the exchanges of anions and ligands between the sheets of the gibbsite of the materials and the humic acid [73,74,75,76,70]. The presence of iron and aluminum oxides in laterite and shale could promote this phenomenon because it seems that higher valence cations such as Fe^{3+}, Al^{3+} could promote more significant sorption of humic acid than lower valence cations [57]. Yuan [25] reported that ligand exchanges between a hydroxyl group attached to aluminum oxides in an allophane structure and a carboxylate group in humic acid would be due to the chemisoption mechanism. Also, Coulibaly [22] showed that chemisorption would be the dominant mechanism during the retention of phosphates on geo-materials such as sandstone, shale, and laterite.

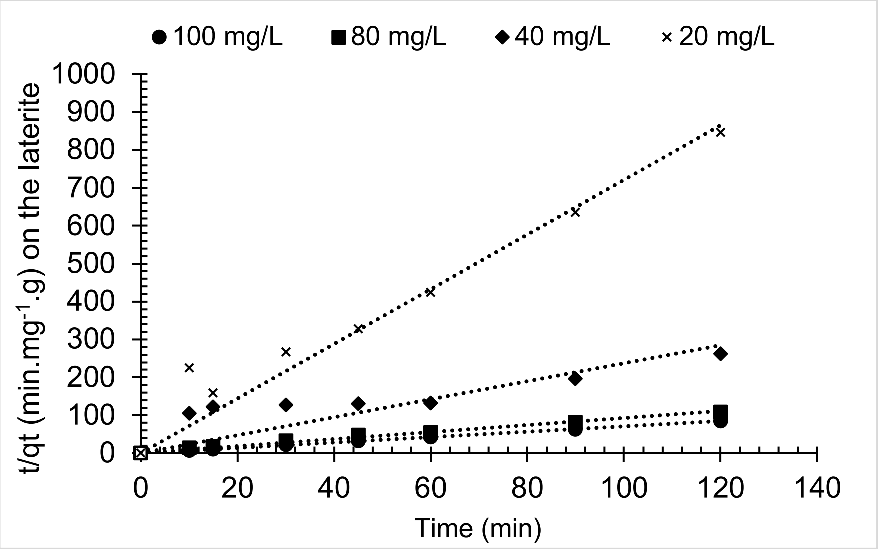

Figure 10: Pseudo-second order linearization for HA adsorption to laterite.

Table II: Parameters of the pseudo-second order model equation.

Parameters / Massive	C_i (mg/l)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2 (min/mg/g)	R	h (mg/g/min)
Latérite	20	0.14	0.14	$2.90\ 10^{-3}$	0.97	$5.80\ 10^{-5}$
	40	0.46	0.42	$9.30\ 10^{-3}$	0.73	$1.90\ 10^{-3}$
	80	1.10	1.07	0.15	0.99	$16.30\ 10^{-2}$
	100	1.42	1.40	0.70	0.99	1.30

3.3.3. Intraparticule diffusion model (Weber and Morris, 1963)

The intra-particle diffusion model applied to the data of the HA adsorption tests on the laterites is presented in **Figure 11**, and the model parameters are entered in **Table III**. Indeed, the curve shows the appearance of two phases: a first linear and one that has become in the form of a plateau, which would indicate that the adsorption process takes place at the surface and intra-particulate diffusion through the micropores. Moreover, the fact that the lines obtained do not go through the origin reveals that the distribution in the pores is involved in the sorption process but is not the only mechanism limiting the kinetics of sorption. Indeed, this result could be due to the fact that the sorption is spanked by trapping in the crystalline pores and the intra-domain regions, and in the intercalated spaces, the physical-chemical nature of the laterite would be more favorable than that of the schist [23,72]. The work of Wu & Gschwend [77] confirms that the sorption kinetics are controlled mainly by the intraparticle diffusion of the solute within microaggregates of soils or sediments.

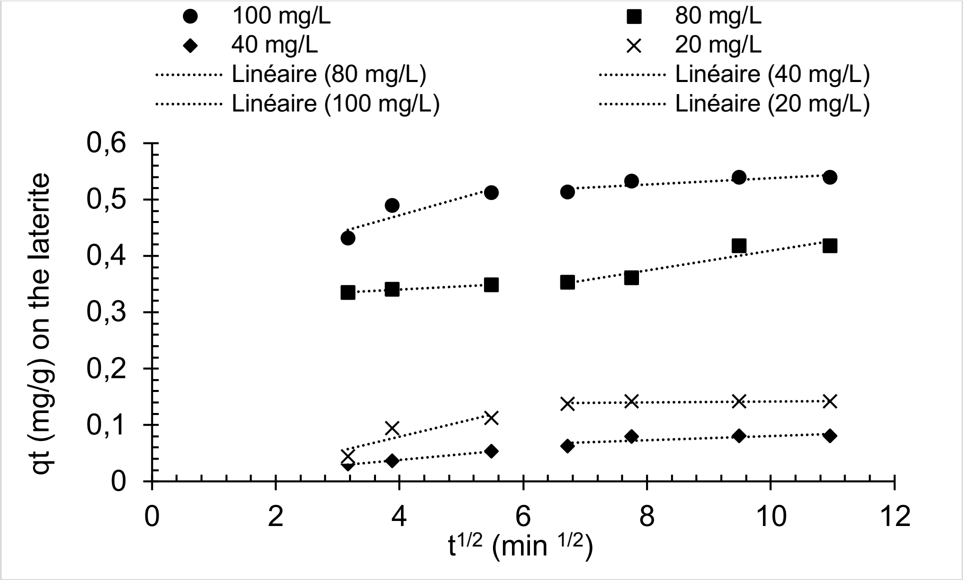

Figure 11 : Linearization according to the intra-particule diffusion model for the adsorption of HA on laterite.

Table III : Intra-particule diffusion parameters on laterite.

Parameters **Massive**	**C_0 (mg/L)**	**k_d (mg/min$^{1/2}$g)**	**C (mg/g)**	**R**
Laterite	20	$2.63\ 10^{-2}$	$2.60\ 10^{-2}$	0.88
	40	0.01	$0.20\ 10^{-2}$	0.99
	80	$0.60\ 10^{-2}$	0.30	0.99
	100	$3.10\ 10^{-2}$	0.35	0.89

3.4. Modeling of adsorption isotherm

3.4.1. Experimental data of adsorption isotherm

Figure 12 shows the adsorption isotherm of humic acid on the laterites. The curve has substantially two phases, the first phase between 0 and 11.5 mg/L of humic acid with an adsorption capacity at equilibrium (qe) equal to 0.92 mg / g on the laterite. Then comes a second visible phase for the treated concentrations. The shape of this curve is of type L according to the classification of Giles [78]. This would mean that the sorption occurs by the progressive occupation of the available sites on the massifs until complete saturation, where retention no longer occurs (sorption in a monolayer). This model (Langmuir) thus makes it possible to predict the number of adsorbate molecules to cover the solid with a single molecular layer.

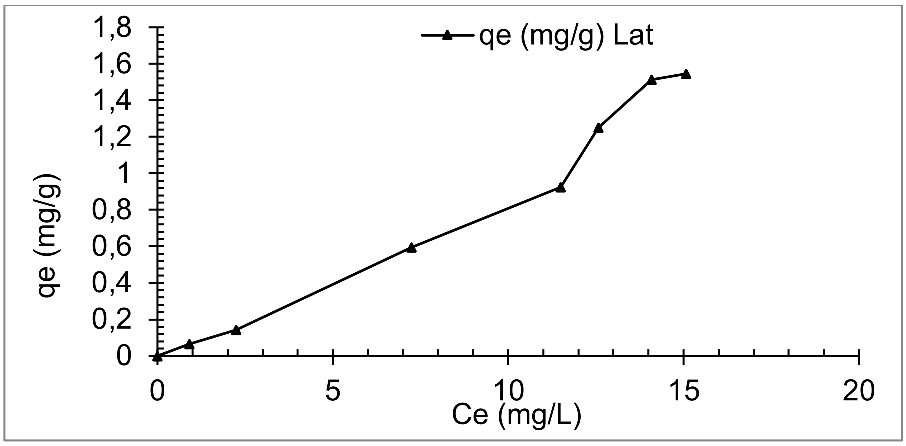

Figure 12: Sorption isotherms of humic acid on laterite

Experimental conditions: initial concentration of humic acid = 15, 20, 40 80, 100 mg / L; Stirring speed = 300 rpm, Stirring time = 90 min; pH = 6.5; Temperature = 26 ° C ± 0.3.

3.4.2. Modeling of the isotherm

The Langmuir and Freundlich models were used to fit experimental data of humic acid sorption on laterite. **Figure 13** plots the 1/qe curve versus 1/ce for the Langmuir model and ln(qe) versus ln(ce) for the Freundlich model. After linearizing the equations, the parameters related to these models are summarized in **Table IV**.

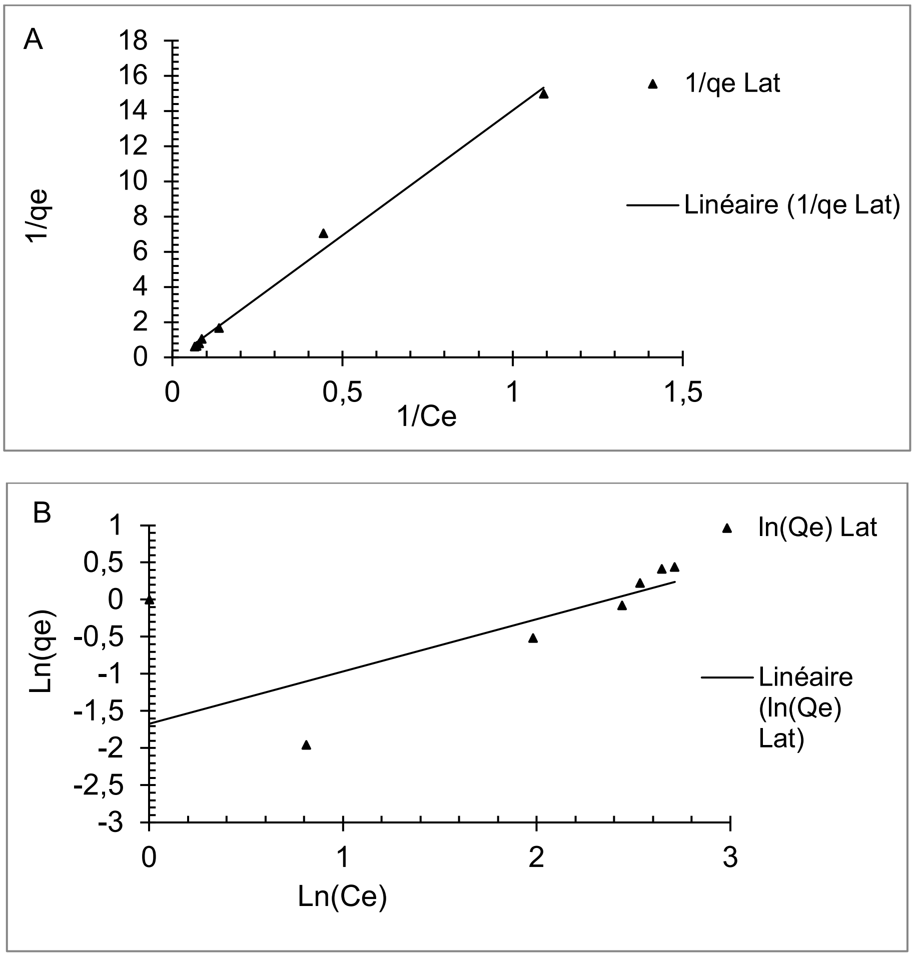

Figure 13: Representation according to the Langmuir (A) and Freundlich (B) model for the adsorption of HA on laterite.

Table IV: Parameters linked to the Langmuir and Freundlich model

Model	Parameters	Laterite
Langmuir	$q_{m,exp}$ (mg/g)	1.50
	$q_{m,L}$ (mg/g)	1.20
	k_L	0.05
	R	0.99
Freundlich	k_f	0.20
	$1/n_f$	0.70
	R	0.70

We notice that the Langmuir and Freundlich models have good affinities because the experimental and theoretical values of Qm obtained are practically identical, and the values of the correlation coefficients are very close to 1. In addition, the Langmuir model showed a better fit with the experimental data of the adsorption isotherms on the two massifs, unlike that of Freundlich [79]. The work of Koua-Koffi [23] on the adsorption of arsenic on laterite, sandstone, and shale noted that the Langmuir model was more satisfactory for describing the adsorption process of As on the three (3) supports. Those of Hengpraprom [80] on the sorption of humic acids (HA) and α-endosulfan by clay minerals gave results similar to those of the present study. By count on montmorillonite, the value of the Freundlich parameter n is less than 1, which indicates that the sorption sites are limited.

Conclusion

The study aims to conduct a batch adsorption treatment of industrial humic acid from laterite. To do this, in order to know the physicochemical nature of the laterite, the mineralogical characterization by XRD and infrared of the laterite was carried out. Results showed the presence of minerals such as iron oxides and oxyhydroxides (hematite (Fe_2O_3), goethite (FeO (OH)), maghemite (Fe_2O_3)), aluminum, calcium, and magnesium in the laterite.

The batch adsorption study demonstrated the optimal concentration of laterite to use. This corresponds to 80 g / L for a concentration of 15 ml / L of humic acid. Regarding the influence of the stirring time on the adsorption of humic acids by the laterite, equilibrium was reached after 90 min on the laterite with absorption maxima of 96 %. Regarding the effect of pH on the adsorption of humic acids on laterite, the results generally showed that the change in masses of adsorbed humic acids is inversely proportional to the increase in pH. The high yield was obtained at a pH between 3.5 and 5.5 with 97.22 % to 93.33 % abatement.

Results of humic acid concentration influence on its sorption on laterite showed an increase in the adsorption efficiency of HA with increasing the initial concentration of HA in solution up to 100 mg/L.

In addition, the Langmuir model showed a better correspondence with the experimental data of the adsorption isotherms on the two massifs, unlike that of Freundlich.

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