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Research Article

Use of Lomo-Nord Shales in Ivory Coast for the Adsorption Treatment of Humic Acid Extracted from Leachate from the Akouédo Landfill

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Abstract

The environmental pollution caused by the mismanagement of household waste dumps and their leachate in developing countries has led researchers to explore adsorption treatment processes using shales from Côte d'Ivoire. To carry out this study, mineralogical characterization by X-ray Diffraction and Infrared of the shales was required prior to treatment. Using humic acid extracted from the leachates, adsorption tests were carried out using batch adsorption tests, and the optimum adsorption parameters were determined and modeled. The results of the mineralogical characterization revealed the presence of certain minerals. Batch adsorption treatment using slate from Côte d'Ivoire showed that the optimum concentration of slate to use was 30 g/L for a concentration of 15 mg/L humic acid. The duration of agitation at equilibrium was 60 minutes, with a maximum adsorption rate of 92 %. The effect of pH on the adsorption of humic acids showed that, in general, the evolution of adsorption rates was inversely proportional to the increase in pH. The highest yields were obtained at pH levels between 3.5 and 5.5. The results of the influence of the initial concentration of humic acids showed an increase in adsorption efficiency with the increase in the initial concentration up to 100 mg/L. The pseudo-second order model better described the adsorption of humic acid on the shale; it is accompanied by intra-particle diffusion, therefore by a contribution of active sites inside the pores.

Keywords

Landfills, Leachate, Shale, Humic Acid, Modeling Adsorption, X-Ray Diffraction, Infrared

1. Introduction

Organic compounds (carbohydrates, proteins, amino acids, lipids and other reserve substances) discharged into aquatic environments degrade chemically and biologically over time [1, 2]. This degradation leads to significant consumption of dissolved oxygen in the water by aquatic organisms, and can result in their asphyxiation [3-5]. In addition, the accumulation of organic compounds in water promotes the enrichment of the aquatic environment with

nutrient salts, hence the phenomenon of eutrophication. This affects aquatic flora and fauna [6]. The result could be the disappearance of some aquatic species and the subsequent death of water bodies.

Humic substances, in general, are naturally present in surface waters with a content of between 1 and 15 mg Carbon. L^{-1}. Unfortunately, due to its high content of organic compounds, leachate has been identified as a potential source of groundwater and surface water pollution [7, 8]. As humic and fulvic acids in leachates are made up of large, high-molecular-weight of molecules such as phenolitic and aromatic compounds, they are a major source of pollution of groundwater and surface water. On average, they make up 30% to 50% of dissolved organic carbon, and in some highly colored waters, up to 90% [9]. As a prelude to the above, photosynthetic activity may be limited in the surface layers of surface waters. Studies carried out by Vigneault [10], on the interaction of dissolved humic substances 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 may also enhance the bioavailability of metals in natural waters.

Futhermore, humic substances may have adverse effects on human health. This is demonstrated by the fact that they are currently causing problems in drinking water treatment plants. They can cause other problems, such as deterioration in organoleptic quality, bacterial growth in distribution network pipes and subsequent corrosion [11, 9, 12]. Also, significant consumption of chlorine during disinfection can also lead to the formation of potentially toxic chlorinated by-products, mainly trihalomethanes and haloacetic acids which at high concentrations would be carcinogenic for humans in the long term [13].

Consequently, leachate must be treated before discharge. Several processes are available for this purpose, but the choice of treatment process depends on the type of leachate. Biological processes are suitable for the treatment of biodegradable leachates, while physico-chemical processes are suitable for leachates with little or no biodegradability. In all cases, the results are satisfactory, but the processes are often costly and require highly skilled labor [14]. As a result, it seems imperative to explore leachate purification technologies that are less costly and adapted to the realities of developing countries such as Côte d'Ivoire [15, 16]. The development of such types of processes could make it possible to mitigate the health and environmental challenges caused by leachates in developing countries.

Many adsorbents have been studied for the treatment of the pollutant load of leachates [17]. They are used for the adsorption of humic substances which constitute the potential organic compounds of the leachate. These adsorbents could thus be classified into two categories. We have biological (bio-adsorbents) and geological (geo-adsorbents) adsorbents. Some research has shown that these adsorbents can be used directly without any prior chemical treatment, which is very economically advantageous [18, 19]. The added value of the study is the valorization of local adsorbents considered as waste in the treatment of another waste such as leachate, by a simple, easy and inexpensive process.

These adsorbents used each have their own more or less broad field of application depending on their specificity. Thus, the adsorption of humic substances on a wide range of mineral surfaces (geomaterials) has been demonstrated and is still the subject of several studies today such as iron oxides and hydroxides; aluminum; manganese, calcite and silica [20-22]. However, the heterogeneous nature of natural organic matter in general, and humic substances in particular, has made it possible to take into account numerous factors (pH, concentration of adsorbents, etc.) to better describe their retention on hydroxides.

It is in this context that the present study intends to develop a system for the treatment of humic acids in the leachate from the Akouédo landfill by adsorption using Lomo-Nord Shale. It would therefore be important to know the optimum parameters influencing adsorption treatment. Specifically, the aim is to characterize the Shale in order to determine their mineralogical composition; to study the adsorption of organic matter from the leachate on the Shale in a closed or batch reactor and to model the adsorption kinetics based on the study data.

2. Materials and Methods

2.1. Materials

2.1.1. Geo-materials or Geo-adsorbents Used

There are two key reasons why Shale were chosen for the Akouédo landfill leachate organic matter treatment trials. Firstly, these endogenous materials are abundant in nature. They are metamorphic rocks characterized by marked schistosity (Figure 1). The specific surface area of Shale is equal to 16.5 m^2/g [23]. Indeed, Shale are metamorphic rocks that were sampled at Lomo-Nord (6°39' 15" N and 4°58' 33" W) in central Côte d'Ivoire, according to the geological map of Côte d'Ivoire adapted by Ouattara [24].
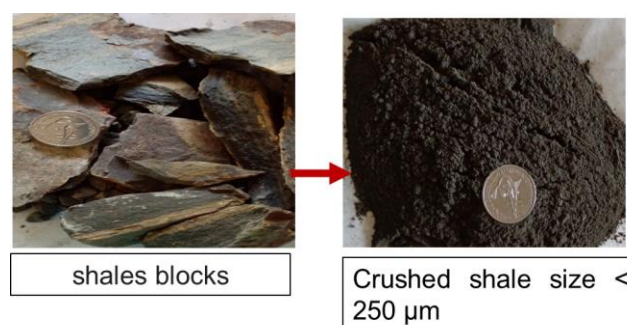

shales blocks

Crushed shale size < 250 μm

Figure 1. Shale blocks and shreds.

2.1.2. Chemicals Used

Sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich® Humic Acid (AH) in France.

2.1.3. Analysis Equipment Used

To characterize the shales, a Bruker D8 Advance diffractometer, operating on a copper anode, was used to identify their mineralogical phases. In addition to the XRD analysis, infrared characterization was carried out using a Brukers Alpha-p spectrometer, equipped with a KBr beam splitter and a TCD detector. A DR 6000 UV-Viscible spectrometer equipped with a 1 cm quartz cell was used to determine the initial and residual concentration of leachates.

2.2. Methods

2.2.1. Sampling and Preparation of Landfill Leachate Solution

Leachate samples were taken at the intersection of the two main leachate streams of the old and new Akouédo landfill (Figure 2), which over an area of 153 ha operated from 1965 until 2017. Despite its closure, these leachates continue to flow under these waste piles [25]. On the samples taken, pH, conductivity and temperature were measured in situ and stored in the laboratory.

On these samples, humic substances were extracted from the leachates [25]. Humic acid solutions were prepared from the pellets obtained during extraction. Starting with distilled water, the pellets were dissolved in a basic medium with 0.05 mol/L sodium hydroxide (NaOH) solution under stirring to obtain a homogeneous solution. The pH of the solution was readjusted with 0.05 mol/L hydrochloric acid (HCl).

Industrial humic acid solutions from Sigma-Aldrich® were prepared for comparison with humic acid extracted from leachate to ensure purity. Next, standards for analysis were obtained by successive dilutions to the desired concentrations, then calibration lines were made from these standards at different pH values. Analyses were carried out using a DR 6000 UV-Visible Spectrometer, in a quartz cell with a path length of 1 cm, at a free wavelength of 800 to 250 nm [26, 27]. This analysis was used to read the absorbance of HA solutions.
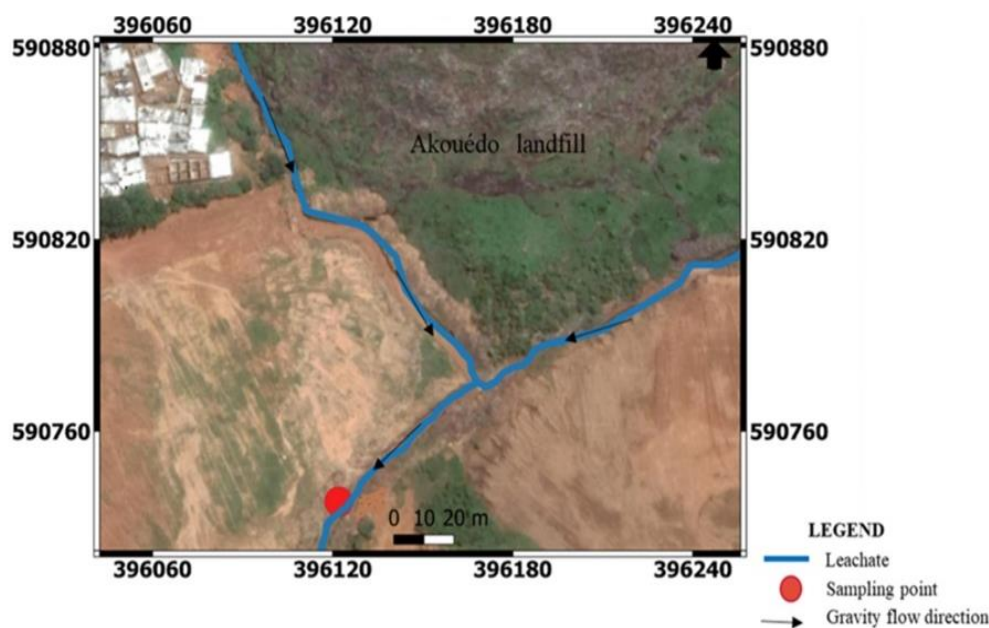

Figure 2. Drainage channels for leachate from the Akouédo landfill [20].

2.2.2. Preparation and Characterization of the Adsorbent Used

The shales blocks collected according to GPS coordinates were washed and steamed, then crushed. The powders obtained using a crusher were sieved using a Saulas sieve (NF.X 11.501) at 250 μm, to be used for DRX and infrared analyses.

X-ray Diffraction (XRD) analyses were carried out on a Bruker D8 Advance spectrometer, operating on a copper anode, at the University of Liège. The analysis consists in subjecting 1 g of powdered shale installed in a capsule to a monochromatic X-ray beam and collecting the diffraction spectrum it emits.

Fourier transform infrared analysis of the shale was done using a Brukers Alpha-p IR spectrometer equipped with a KBr beam splitter and a TCD detector at the Laboratory of Applied Inorganic Chemistry of University of Yaoundé I. Measurements were carried out in diffuse reflection with a

mass of 2 mg of shale sample powder. The shales powder was mixed with 300 mg of potassium bromide to attenuate energy losses. Absorption spectra were produced in absorbance mode, with a scanning wavelength ranging from 4000 to 400 cm^{-1}. They reveal the presence of specific atomic groups in a given phase.

2.2.3. Optimization of Humic Acid Adsorption Parameters on Shales

As batch tests are closed systems, they enable maximum adsorption conditions to be obtained. Adsorption tests were carried out on shale crushed in contact with leachate solutions. To this end, the 15 mg/L Humic Acid (HA) solution was prepared from the leachate stock solution and stirred in 200 mL Erlenmeyer flasks at 26 ℃ ± 0.3 using magnetic stirring at 300 rpm.

On the shale adsorbents, the optimum parameters - adsorbent mass, stirring time, medium pH and adsorbate concentration - were determined.

(i). Determination of Adsorbent/Adsorbate Ratio (Optimal Dose of Shale)

To find the optimum shales mass, shred quantities were varied in 0.1 g increments and mixed each time with 50 mL of the leachate solution (Figure 3). After stirring, the solutions were centrifuged at 4000 rpm for 15 min. The filtrates obtained were analyzed by the DR 6000 Spectrometer to monitor the abatement of HA in solution. Abatement rates were calculated according to relationship 1.

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

With: C0 (mg/L) the initial HA concentration and Ct (mg/L) the residual concentration.
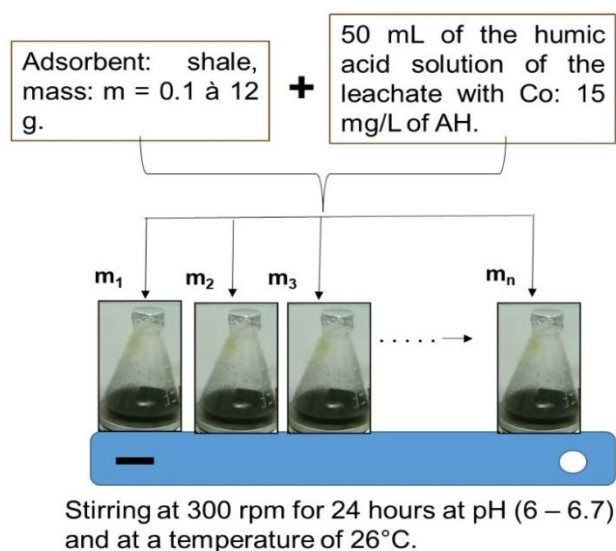

Figure 3. Stage in the search for the optimum dose of shale.

(ii). Adsorption Kinetics and Influence of Initial HA Concentration

The kinetic study of the adsorption of the organic matter present in the leachate on the shales enables us to determine the rate of fixation of the organic matter on these masses and the equilibrium adsorption capacities of the shale with respect to the organic matter, on the one hand, and to model the kinetics in order to determine the characteristic adsorption parameters, on the other.

Starting with the optimum mass of shales, the stirring time was varied in 10 min steps for 1 h, then in 60 min steps until saturation of the materials was reached. Residual HA concentrations were determined at each time step and the removal rate was calculated according to relation 1 above.

During these kinetic tests, the concentration of leachate was varied from 20, 40, 80 to 100 mg/L at the pH of the medium (6-6.7) at the optimum values of mass and stirring time obtained under the same reaction conditions described above. These experiments determined the adsorption capacity (Qt) of the shale. The residual concentrations of HA in solution measured enable us to deduce the quantity of organic matter retained at each instant t (Qt). The quantity of organic matter per unit mass of shale at time t is determined by the following relationship (2):

$$Q_{ads} = \frac{C_0 - C_t}{m} x V \qquad (2)$$

With: Qads (mg/g), adsorption capacity after stirring time t; Ct, AH concentration at time t (mg/L); Co, initial AH concentration (mg/L); m, shale mass (g) and V, solution volume (L).

(iii). Determining the Optimum pH

The influence of the pH of the reaction medium on the adsorption of organic matter onto shale was determined at different pH levels (3.5; 4.5; 6.5; 8.5 and 9.5) under the same reaction conditions as above. The pH was adjusted using 0.1 M hydrochloric acid or 0.1 M sodium hydroxide. Residual HA concentrations were determined at equilibrium and the abatement rate was calculated according to relation 1 above.

2.2.4. Modeling Adsorption Kinetics

The mechanism of humic acid adsorption can be explained using kinetic models, which provide information on the dynamics of the adsorption process in terms of order and rate constant. These are important for designing and modeling an efficient adsorption operation.

Among the models used to model adsorption kinetics by researchers, three kinetic models were used in this study, including two reaction models (pseudo first-order and pseudo second-order) [28, 23, 29] and one diffusion model (Weber and Morris intra-particle diffusion) [23, 30]. The kinetic equations and their linearized forms of the models are thus developed according to equations 3, 4, 5 and 6.

(i). Pseudo-first Order: qe, k_1

$$log(qe - qt) = log(qe) - \left(\frac{k_1}{2,303} * t\right) \qquad (3)$$

With: qe and qt, the quantity of solute adsorbed at equilibrium and time t respectively (mg/g); k_1, the adsorption rate constant (min^{-1}).

The quantity of solute adsorbed at equilibrium qe and the pseudo-first-order rate constant k_1 are determined from the plot of Log $(qe - qt)$ versus time t.

(ii). Pseudo Second-order: qe, k_2

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

$$h = k_2 q_e^2 \qquad (5)$$

Where: k_2, rate coefficient (g.mg^{-1}min^{-1}); h, initial adsorption rate.

Plotting $\frac{t}{qt}$ against time t gives a linear curve with a slope of $\frac{t}{Q_e}$ and an intercept of $\frac{1}{k_2 q_e^2}$.

(iii). Diffusion Adsorption Model: Intra-particule Scattering kd, C.

$$q(t) = k_d t^{1/2} + C \qquad (6)$$

With: k_d mg/(g.h$^{1/2}$): the intra-particle diffusion constant, C (mg/g): constant representative of thickness, k_d depends on the diffusion coefficient of the species in question, as well as the size and number of pores in the adsorbent material.

3. Results

3.1. Characteristic of Shale

Figure 4A shows the spectra resulting from XRD analysis of the shale crushed material. This analysis highlights the presence of six minerals at certain intensities, including Muscovite (KAl$_2$Si$_3$AlO$_{10}$(OH)$_2$), Chlorite (Mg$_6$Si$_4$O10(OH)$_8$), Albite (Na(AlSi$_3$O$_8$)), Kaolinite ((Si$_2$O$_5$Al$_2$(OH)$_4$), Dolomite (CaMg(CO$_3$)$_2$) and Quartz (SiO$_2$).

Infrared analysis (FTIR) is a mineralogical analysis tool that complements X-ray Diffraction, and the infrared spectra of schists are shown in Figure 4B.

The spectra reveal the presence of four (4) main minerals: kaolinite, chlorite, quartz and albite. Bands 3696, 3620, 1123 and 913 cm^{-1} are attributed to symmetrical elongation vibrations from free OH groups on the external surface, elongation vibrations from internal OH groups and deformation δOH (internal) linked to kaolinite. As for chlorite, this is represented by the elongation vibration of its vOH group at 3596 cm^{-1}. Vibrations at 778 and 695 cm^{-1} are Si-O elongation vibrations and its harmonics attributed to quartz. Finally, the vibration band at 649 cm^{-1} is attributed to albite-related SiO deformation.
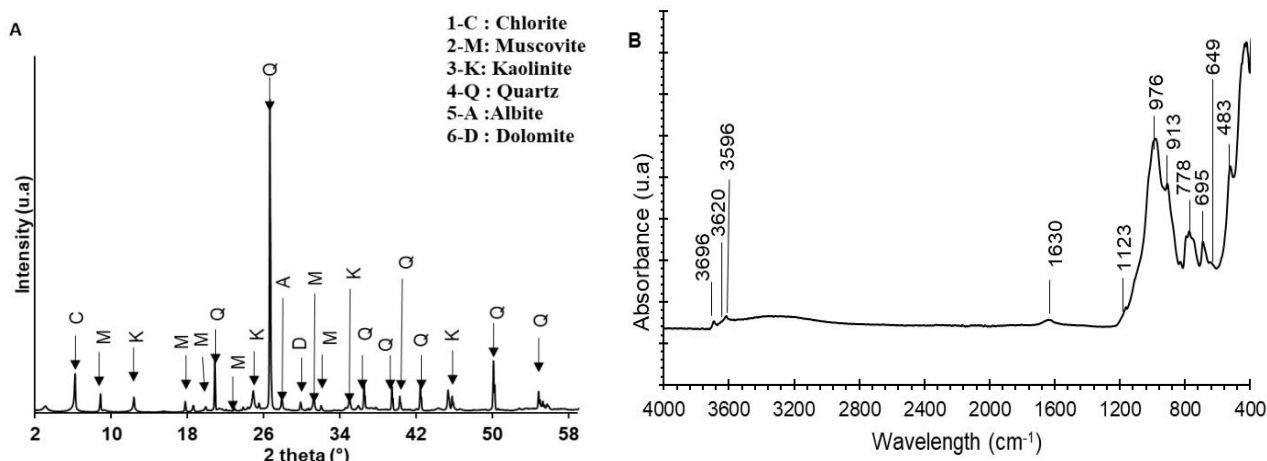
Figure 4. X-ray spectra of shale (A) and Infrared spectrum of raw shale between 4000 and 400 cm^{-1} (B).

3.2. Characteristic of Humic Acid in Leachate Compared with Industrial Humic Acid

In order to determine the nature of the humic acid in the leachate, a comparison was made between industrial humic acid and that extracted from the leachate. UV-Visible spectra of both solutions were carried out and are shown in Figure 5. The spectra show a decrease in absorption intensity with increasing wavelength. However, in all spectra of industrial humic acid and leachate, a peak is observed at 286 nm. Also, a shoulder was revealed around 250-300 nm.
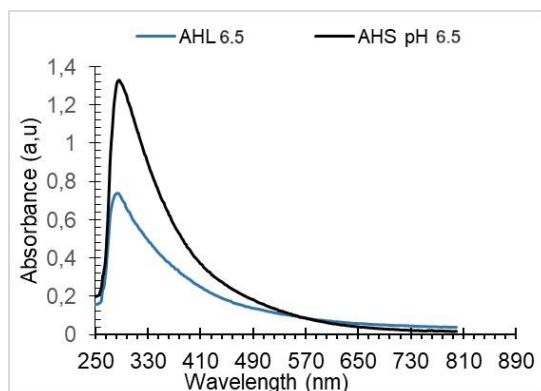
Figure 5. *UV spectra of synthetic humic acid (SHA) and leachate humic acid (LHA) at pH 6.5.*

3.3. Optimum Parameters Adsorption of Humic Acid from Leachate on Shales

3.3.1. Influence of Adsorbent Mass, Optimal Contact Time, Effect of Ph and Influence of the Initial Humic Acid Concentration

The evolution of humic acid removal rates from leachate as a function of shale mass (g/L) is shown in Figure 6A. The curve shows three (3) phases, a first steep phase where the curve reaches a removal rate of 79.40 %, followed by a second shallow phase with removal rates peaking at 90 % removal with increasing shale mass. Finally, the third phase shows a slight regression, with yields decreasing as shale mass increases. The corresponding yields range from 90 % to 81.02 %.

Figure 6B shows the evolution of humic acid removal rates from leachate as a function of agitation time. The curve shows two phases, one increasing and the other stationary. Equilibrium is reached at 60 minutes, with a maximum adsorption rate of 92.22 %. The second phase remains stationary regardless of the increase in stirring time.

These relatively short contact times highlight the speed with which humic acid functional groups interact with the oxides present on shale mineral surfaces.

The effect of pH on the adsorption of humic acid from leachate by shale was monitored at different environmental pH values. Figure 6C shows humic acid removal rates as a function of pH. It can be seen that abatement rates are inversely proportional to increasing pH. As a result, in acidic environments, i.e. in the range 3.5 < pH < 5.5, these rates are high, with values between 95.60 % and 90.90 %. Above pH 5.5, i.e. from pH 6.5 to 9.5, abatement rates decrease with increasing medium pH, ranging from 61.70 % to 36.10 %.

Figure 6D shows the effect of initial humic acid concentration in the leachate on the adsorption capacity of the shale. It can be seen that the adsorption capacities obtained, respectively 0.08, 0.17, 0.43 and 0.54 mg/g for initial concentrations of 20, 40, 80, 100 mg/L, change with increasing initial concentration. The higher the initial humic acid concentration, the greater the quantity of functional groups adsorbed, offering more binding sites.
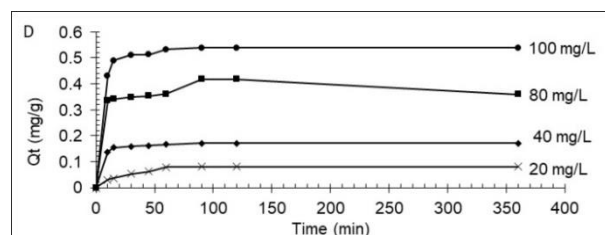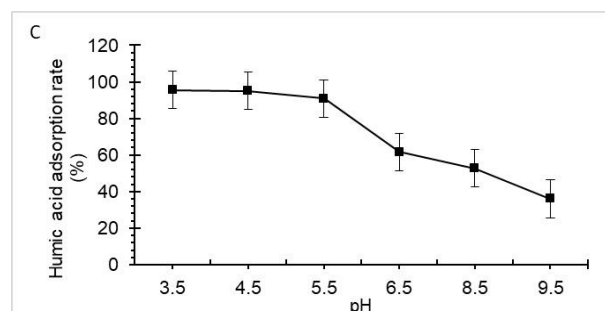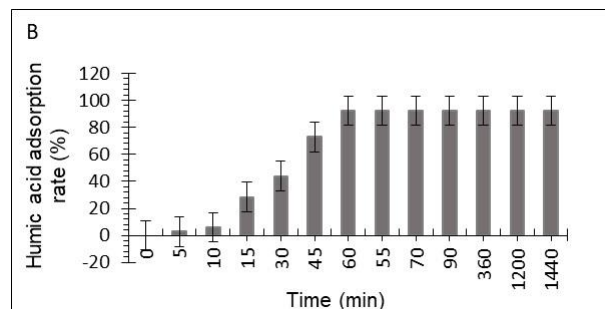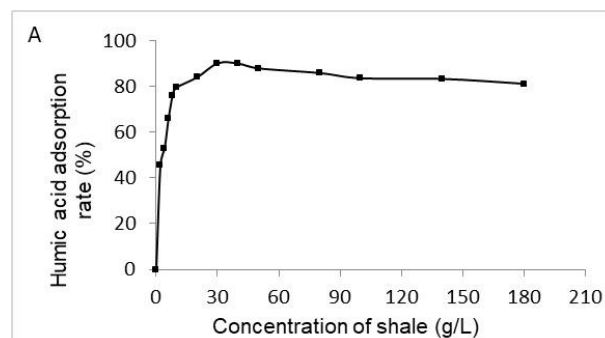
Figure 6. *Optimum shale concentration curve (A), Effect of contact time (B), Effect of pH on the adsorption (C) and Effect of initial humic acid concentration (D).*

3.3.2. Modeling Adsorption Kinetics: Pseudo-first-order, Pseudo-second-order Model and Intra-particle Diffusion Model

The experimental data obtained as a function of time were analyzed using pseudo-first-order and pseudo-second-order kinetic models. Figure 7 shows the application of pseudo-first-order (A) and pseudo-second-order (B) kinetic models to experimental data at different initial humic acid concentra-
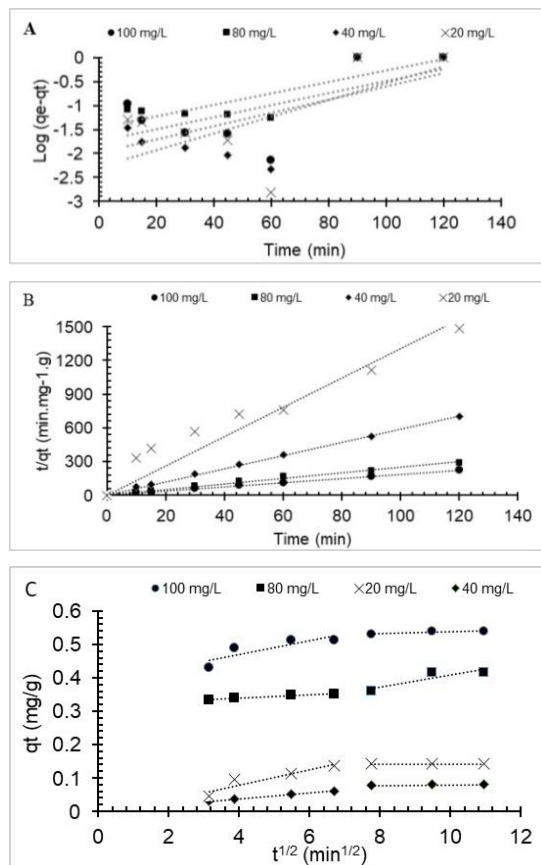
tions. The constant parameters of the kinetic equation and the values of the correlation coefficients are summarized in Table 1. It can be seen that the values of the correlation coefficients (R) obtained with the pseudo-second-order model tend towards 1. It can be seen that the values of the correlation coefficients (R) obtained with the pseudo-second-order model tend towards 1. Also, the values of q(Qe.cal, mg/g) determined by the pseudo-second-order model were in perfect agreement with the experimental results q(Qe,exp, mg/g) in contrast to those of the pseudo-first-order kinetic model (Table 1).

Figure 7C shows the application of the intra-particle diffusion model to experimental data at different initial humic acid concentrations in the leachates. Table 2 summarizes the model parameters. Whatever the humic acid concentration, the curves show two phases, a linear first phase and a plateau-shaped second. This would indicate that the adsorption process takes place on the surface and by intra-particle diffusion through the micropores. The second stage was intraparticle diffusion, which slowed down and reached equilibrium. Also, the values of the correlation coefficients (R) tend towards 1.

Table 1. Pseudo first- and second-order model equation parameters.

C_i (mg/L)	Pseudo first order model					Pseudo second order model			
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (min^{-1})	R		$q_{e,cal}$ (mg/g)	k_2 (min/mg/g)	R	H (mg/g/min)
20	0.08	0.60	$1.70\ 10^{-3}$	0.57		0.03	16.50	0.94	0.11
40	0.17	0.70	$3.30\ 10^{-3}$	0.73		0.17	$2.60\ 10^{-2}$	0.99	$7.70\ 10^{-4}$
80	0.42	1.10	$5.30\ 10^{-3}$	0.83		0.40	0.20	0.99	$4.20\ 10^{-2}$
100	0.54	1.10	$7.70\ 10^{-3}$	0.62		0.51	2.00	0.99	0.60

Table 2. Intra-particle diffusion parameters on shale.

C_0 (mg/L)	k_d (mg/min$^{1/2}$g)	C (mg/g)	R
20	$2.30\ 10^{-2}$	0.01	0.93
40	$0.90\ 10^{-2}$	$0.1\ 10^{-2}$	0.99
80	$0.50\ 10^{-2}$	0.30	0.99
100	$0.20\ 10^{-2}$	0.50	0.85

4. Discussion

These DRX and IR analyses of shales revealed that they are abundant in minerals such as aluminum, silica and magnesium oxides and hydroxides. The presence of these minerals in schists is thought to be due to the fact that they are altered metamorphic or sedimentary or eruptive rocks [31, 23]. Indeed, metamorphic rocks result from intense alteration of any pre-existing rock by heat and/or pressure and/or chemical change. Thus, these results provide us with information on the mineralogical nature of shales, which would be an asset when trying to treat humic substances in leachate by adsorption [32, 33].

In order to determine the nature of the humic acid in the leachate, a comparison was made between industrial humic acid and that extracted from the leachate. The spectra show a decrease in absorption intensity with increasing wavelength. However, in all spectra of industrial humic acid and leachate,

Figure 7. Pseudo-first-order (A), second-order (B) and Intra-particle diffusion model (C) linearization for HA adsorption on shale.

a peak is observed at 286 nm. Also, a shoulder was revealed around 250-300 nm. This could be linked to the fact that humic acid possesses chromophores, and the observed shoulder could be attributed to the presence of aromatic structures. Studies by Fooken and Liebezeit [34] and Niu *et al.* [35] have shown that this shoulder is due to the overlapping absorbance of a large number of chromophores present in the core of the humic acid molecule.

In general, the chromophores responsible for absorption in this UV region are mainly phenolic arenes, benzoic acids, aniline derivatives, polyenes and polycyclic aromatic hydrocarbons with two or more rings [26, 27]. The presence of OH bonds from alcohol groups, phenols, carboxylic acids and aromatic C=C bonds had been revealed in humic acids from leachate by studies by Coulibaly *et al.* [25]. These would confirm the purity of humic acids extracted from leachate and their similarity to industrial humic acids.

The evolution of humic acid removal rates from leachate as a function of shale mass (g/L) is shown three (3) phases. The yields obtained in these three phases are justified by the availability of adsorbent surfaces. Thus, as the mass of shale in the reaction medium increases, the yield increases until it is parked, hence the slowdown observed in the second phase. This can be explained by the fact that, as the quantity of shale in the medium increases, the formation of deposits of material due to the production of agglomeration occurs [36, 37]. Thus, from a given concentration of materials (optimum concentration), any further addition of materials does not contribute to adsorption [38, 23].

The curve of the evolution of humic acid removal rates from leachate as a function of agitation time shows two phases, one increasing and the other stationary. Equilibrium is reached at 60 minutes.

These relatively short contact times highlight the speed with which humic acid functional groups interact with the oxides present on shale mineral surfaces. Indeed, some studies have shown that the adsorption kinetics of organic pollutants in soils is a rapid phenomenon where often more than 50 % of the solute is adsorbed in a few minutes [39]. Thus, a few hours of contact would suffice to reach equilibrium. The adsorption of organic compounds such as humic substances depends not only on their affinity for the adsorbent, but also on interactions with the solvent itself [40, 41].

The effect of pH on the adsorption of humic acid from leachate by shale was monitored at different environmental pH values. It can be seen that abatement rates are inversely proportional to increasing pH. The high rate of adsorption of humic acid from leachate by shale in an acidic environment is due to the reaction between the carboxylic, aromatic and phenolic functions of humic acids and the mineral surface of the shale. Indeed, the main minerals present in shale, such as aluminum, silica and magnesium oxides and hydroxides, can be considered as reactive surfaces [42, 33]. Also, the chemical reactivity of minerals is linked to their surface properties, yet the surface charges of shales are negative

whatever the pH of the environment [43]. According to Daifullah *et al.* [44], at low pH, a greater number of functional groups (COOH, OH, NH_2, etc.) are in an uncharged state, making them more adsorbable. Also, at low pH, the zeta potential of humic acid remained negative, favoring the adsorption of humic acid onto protonated surfaces by ligand exchange [20, 45]. Ligand exchange favors interactions, hence the high adsorption rate.

On the other hand, in a basic environment, the decrease in adsorption rates observed is justified by the fact that the surface charge of the shale is negative, which limits interactions with humic acid functional groups [46].

Figure 6D shows the effect of initial humic acid concentration in the leachate on the adsorption capacity of the shale. The higher the initial humic acid concentration, the greater the quantity of functional groups adsorbed, offering more binding sites. This result is supported by those of Zhang *et al.* [47], who showed that the adsorption of fulvic acid and humic acid on smectite and vermiculite increased with increasing ionic strength. The adsorption capacity of humic acid from leachate by shale is strongly related to the increase in driving force and concentration gradient [23, 41, 48].

Contrary to these results, the Studies by Achour and Seghairi [49] on the adsorption of synthetic humic substances on bentonite showed that bentonites have variable efficiency linked to the concentration gradient. Indeed, yields decreased from 55.55 to 24.85 % with the contents of humic substances from 5 to 15 mg/L and the masses of bentonite introduced from 50 to 1600 mg.

Indeed, the effectiveness of clays depends on their mineralogy, their specific surface area and their high cation exchange capacity. These determine the extent of the soil reactivity surface with humic substances [17].

The work of Gueu [50] on the elimination of humic acids present in water by adsorption and/or photocatalysis from three raw clays which come from Dabou, Yamoussoukro and Katiola in Ivory Coast, revealed that the clay richest in kaolinite (that of Yamoussoukro) has a much higher maximum adsorption capacity (115 mg/g) compared to the others. (20 and 15 mg/g for Dabou and Katiola respectively).

The experimental data obtained as a function of time were analyzed using pseudo-first-order and pseudo-second-order kinetic models.

These values obtained show that the pseudo-second-order model better describes the kinetics of humic acid adsorption from leachates by shales. Consequently, this model could be used for the adsorption process of humic acid from leachates. Also, chemisorption could be the dominant mechanism in humic acid adsorption on shale [23, 51, 52].

The application of the intra-particle diffusion model to experimental data at different initial humic acid concentrations in the leachates, illustrates that whatever the humic acid concentration, the curves show two phases, a linear first phase and a plateau-shaped second. This would indicate that the

adsorption process takes place on the surface and by intra-particle diffusion through the micropores [23].

The second stage was intraparticle diffusion, which slowed down and reached equilibrium. Also, the values of the correlation coefficients (R) tend towards 1. However, the fact that the straight lines obtained do not pass through the origin, reveals that the process of sorption of humic acid by shale occurs diffusion in the pores but, is not the only limiting mechanism of sorption kinetics [23, 43, 48].

5. Conclusions

In order to carry out a study of humic acid batch adsorption treatment of leachate from slate shales in Côte d'Ivoire, DRX and Infrared mineralogical characterization of the shale was carried out prior to treatment, to determine its physico-chemical nature. The results of this analysis revealed the presence of a number of minerals, including Muscovite $(KAl_2Si_3AlO_{10}(OH)_2)$, Chlorite $(Mg_6Si_4O10(OH)_8)$, Albite $(Na(AlSi_3O_8))$, Kaolinite $((Si_2O_5Al_2(OH)_4)$, Dolomite $(CaMg(CO_3)_2)$ and Quartz (SiO_2).

The presence of these mineral phases could be conducive to interactions with the molecular functions of humic acids.

With regard to the actual treatment of humic acid in leachate by batch adsorption using slate from Côte d'Ivoire, the study showed that the optimum concentration of slate to use corresponds to 30 g/L for a concentration of 15 mg/L of humic acid. Regarding the influence of stirring time, equilibrium was reached after 60 minutes, with a maximum adsorption rate of 92 %. Concerning the effect of pH on the adsorption of humic acids on slate shale, the results showed that, in general, the evolution of adsorption rates was inversely proportional to the increase in pH.

Significant yields were obtained at pH values between 3.5 and 5.5. Relative results on the influence of initial humic acid concentration showed an increase in HA adsorption yield with increasing initial concentration up to 100 mg/L.

Modelling of the data showed that the pseudo-second-order model best describes the adsorption of humic acid on shale, hence the existence of chemisorption. This study is accompanied by intra-particle diffusion and thus the contribution of active sites within the pores.

This study allowed us to understand through these adsorption tests that slate can be used for the treatment of leachate from household waste landfills in general and humic acids in particular.

Abbreviations

C	Carbone
GPS	Global Positioning System
FTIR	Fourier Transform InfraRed Spectroscopy
HA	Humic Acid
N	North
pH	Potentiel Hydrogène
TCD	Thermal Conductivity Detector
UNESCO	United Nations Educational, Scientific and Cultural Organization
XRD	X-ray Diffraction
W	West

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Author Contributions

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Ethics Approval and Consent to Participate

The study was approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out.

Data Availability Statement

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

Conflicts of Interest

The authors declare no conflicts of interest.

References

[1] Gruau, G.; Birgand, F.; Jardé, E.; Novince, E. Pollution des captages d'eau brutes de Bretagne par les Matières Organiques. Rapport de synthèse du groupe d'Etude sur la Pollution des eaux par les Matières Organiques. 2004, 108 p. www.geosciences.univ-rennes1.fr/ch/gruau/MO/GEPMO.htm

[2] Conseil Scientifique de l'Environnement de Bretagne. FICHES TECHNIQUES & SCIENTIFIQUES : Pour la compréhension des bassins versants et le suivi de la qualité de l'eau. 2005, 21p. https://www.creseb.fr/voy_content/uploads/2021/04/Recueil-Fiches_FamilleB_MatOrg_CSEB2005.pdf Consulté le 22 novembre 2024.

[3] Gruau, G.; Birgand, F.; Novince, E.; Jardé, E. Pollution des captages d'eau brute de Bretagne par les matières organiques. Rapport de synthèse. Tableau de bord de la pollution. Causes possibles. Recommandations. Rapport Drass et région Bretagne, 2004b, 108 p. https://irsteadoc.irstea.fr/oa/PUB00016536-pollution-des-captages-eau-brute-bretagne-par-les.html

[4] Seo, DJ.; Kim, YJ.; Ham, SY.; Lee, DH. Characterization of dissolved organic matter in leachate discharged from final disposal sites which contained municipal solid waste incineration residues. J. Hazard. Mater., 2007, 148(3): 679-692.

[5] Adjiri, O. A.; Gone, D. L.; Kouame I. K.; Kamagate, B.; Biemi, J. La caractérisation de la pollution chimique et microbiologique de l'environnement de la décharge d'Akouédo, Abidjan (Côte d'Ivoire). Int. J. Biol. Chem. Sci., 2008, 2(4): 401-410.

[6] Ministère de la Transition Ecologique et Solidaire. Guide technique relatif à l'évaluation de l'état des eaux de surface continentales (cours d'eau, canaux, plans d'eau). Directive 2000/60/CE du 23 octobre 2000 du Parlement européen et du Conseil établissant un cadre pour une politique communautaire dans le domaine de l'eau. 2019, 123 p. https://cpepesc.org/wp-content/uploads/2020/12/Guide-relatif-%C3%A0-l%E2%80%99%C3%A9valuation-de-l%E2%80%99%C3%A9tat-des-eaux-de-surface-continentales.pdf Consulté le 22 novembre 2024.

[7] Birgand, F. ; Novince, E.; Gruau, G.; Bioteau, T. Facteurs expliquant la présence de matières organiques dans les eaux superficielles en Bretagne. Rapport du Cemagref. Groupe d'Etude sur la Pollution des eaux par les Matières Organiques. 2004, 78 p.

[8] Turki, N.; Belhaj, D.; Jaabiri, I.; Ayadi, H.; Kallel, M.; Bouzid, J. Determination of Organic Compounds in Landfill Leachates Treated by Coagulation-Flocculation and Fenton-Adsorption. J. Environ. Sci. Toxicol. Food Technol., 2013, 7 (3/18-25): 2319-2402.

[9] Emilien, B. Évolution de l'impact environnemental de lixiviats d'ordures ménagères sur les eaux superficielles et souterraines : approche hydrobiologique et hydrogéologique de la décharge d'Etueffont. Thèse de Doctorat, Université de Franche-Comté, Besançon, France, 2008, 248 p.

[10] Vigneault, B. Interactions des substances humiques dissoutes avec les algues unicellulaires - Mécanismes et implications. Thèse de Doctorat, Université de Quebec INRS -Water, Quebec, Canada, 2000, 164 p.

[11] Maiga, A. S. Qualité organoleptique de l'eau de consommation produite et distribuée par l'EDM. sa dans la ville de Bamako : évaluation saisonnière. Thèse de Doctorat à l'Université de Bamako, Bamako, Mali, 2005, 77 p.

[12] Goné, DL (2010). Matières organiques naturelles dans les eaux de surfaces du bassin versant de l'Agneby : Caractérisation et élimination par coagulation-floculation au cours de la production d'eau potable. Thèse de Doctorat d'Etat, Université Nangui Abrogoua, Abidjan, Côte d'Ivoire, 2010, 257 p.

[13] Le chevallier, M. W. Coliform regrowth in drinking water: A review J. AM. Water Work. Assoc., 1990, 82 (11): 74-86.

[14] Souhaila, T. Études de traitement des lixiviats des déchets urbains par les Procédés d'Oxydation Avancé photochimiques et électrochimiques de la décharge tunisienne "Jebel Chakir" Thèse de Doctorat à l'Université Paris-Est, Paris, France, 2012, 225 p.

[15] United Nations Environment Program. Africa Environment Outlook: Past, present and future perspectives. 2002, 19 p. http://www.unep.org/dewa/Africa/publications/AEO % 2D1. Consulté le 17 janvier 2019.

[16] Henze, M. et Ujang, Z. Sustainable Sanitation for Developing Countries. In Henze. M., Ujang Z. (Eds). Municipal wastewater Management in Developing Countries: Principles and Engineering. International Water Association (IWA) Publishing, London, England, 2006, 364 p. https://www.amazon.com/Municipal-Wastewater-Management-Developing-Countries/dp/1843390302

[17] Zalaghi, A., Lamchouri, F., Toufik, H., & Merzouki, M. Valorisation des matériaux naturels poreux dans le traitement des Lixiviats de la décharge publique non contrôlée de la ville de Taza, Maroc. J. Mater. Environ. Sci., 2014, 5 (5): 1643-1652.

[18] Claret, F., Schäfer, T., Brevet, J., Reiller, P. E. Fractionation of Suwannee River fulvic acid and Aldrich humic acids on α-Al_2O_3: spectroscopic evidence. Environ. Sci. Technol., 2008, 42: 8793-8809.

[19] Bennama, T., Abdelkader, Y., Zoubir, D., Abdelkader, D. Caractérisation et traitement physico-chimique des lixiviats de la décharge publique d'El-Kerma par adsorption en discontinu sur de la sciure de bois naturelle et activée chimiquement. Water Qual. Res. J. Can. 2010, 45(1): 81-90.

[20] Reiller, P., Moulin, V., Casanova, F., Dautel, C. Retention behaviour of humic substances onto mineral surfaces and consequences upon thorium (IV) mobility: case of iron oxides. Appl. Geochem., 2002, 17: 1538-1551.

[21] Tan, X. L., Wang, X. K., Geckeis, H., and Rabung, T. H. Sorption of Eu(III) on Humic Acid or Fulvic Acid Bound to Hydrous Alumina Studied by SEM-EDS, XPS, TRLFS, and Batch Techniques. Environ. Sci. Technol., 2008, 42: 6532-6537.

[22] Zhao, G., Li, E., Li, J., Xu, M., Huang, Q. and Rong, X. Effects of Interfaces of Goethite and Humic Acid-Goethite Complex on Microbial Degradation of Methyl Parathion. Front. Microbiol., 2018, 9, 1748.

[23] Coulibaly, S. L.; Yvon, J.; Coulibaly, L. Physicochemical Characterization of Lomo Nord black shale and application as low cost material for phosphate adsorption in aqueous solution. J. Environ. Earth Sci., 2015, 5: 42-60.

[24] Ouattara, G. Structure du batholite de Ferkessédougou (secteur de Zuénoula, Côte-d'Ivoire) : Implications sur l'interprétation du paléoprotérozoïque d'Afrique de l'ouest à 2.1 Ga. Thèse Doctorat, Université d'Orléans, Orléans, France, 1998, 291 p.

[25] Coulibaly, Y.; Koné, T.; Kamagaté, M.; Ouattara, P. J-M.; Coulibaly, S. L.; Coulibaly, L. Characterization of the Leachate from the Municipal Landfill of Akouédo (Abidjan, Côte d'Ivoire). J. Environ. Earth Sci., 2020, 10(4): 17-22.

[26] Cunha, T. J. F.; Novotny, E. H.; Madari, B. E.; Martin-Neto, L.; Rezende, M de O.; Canelas, LP.; Benites, V de M. Spectroscopy Characterization of Humic Acids Isolated from Amazonian Dark Earth Soils (Terra Preta De Índio). (eds.), Amazonian Dark Earths: Wim Sombroek's Vision, 2009, 10 p. https://core.ac.uk/download/pdf/45486839.pdf consulté le 22 08/2021.

[27] Giovanela, M.; Crespo, JS.; Antunes, M.; Adametti, DS.; Fernandes, AN. Chemical and spectroscopic characterization of humic acids extracted from the bottom sediments of a Brazilian subtropical microbasin. J. Mol. Struct., Elsevier, 2010, 981(1-3): 111-119.

[28] Sun, L M. et Meunier, F. Adsorption. Aspects théoriques. Techniques de l'Ingénieur, 2003, 2: 1-20.

[29] Ho Y. S, McKay G. Pseudo-second-order model for sorption process. *Process Biochemistry*, 1999, 34: 451–465.

[30] Tunali S, Özcan AS, Özcan A, Gedikbey T. Kinetics and equilibrium studies for the adsorption of Acid Red 57 from aqueous solutions onto calcined-alunite, *J. Hazard. Mater.* 2006, 135: 141–148.

[31] Ama, A. B. Gestion des eaux usées domestiques : caractérisation en réseau et prétraitement à l'aide d'un filtre à sable à alimentation intermittente. Thèse de Doctorat, Université NANGUI ABROGOUA, Abidjan, Côte d'Ivoire. 2013, 138 p.

[32] Kögel-Knabner, I.; Guggenberger, G.; Kleber, M.; Kandeler, E.; Kalbitz, K.; Scheu, S.; Eusterhues, K.; Leinweber, P. Organo-mineral associations in temperate soils: Integrating biology, mineralogy, and organic matter chemistry. J. Plant Nutrition and Soil Sci., 2008, 171: 61- 82.

[33] Khansaa, Al-E and Fawwaz, K. Adsorption of Humic Acid onto Jordanian Kaolinite Clay: Effects of Humic Acid Concentration, pH, and Temperature. Sci. J. Chem., 2018, 6(1): 1-10. https://doi.org/10.11648/j.sjc.20180601.11

[34] Fooken, U. et Liebezeita, G. Distinction of marine and terrestrial origin of humic acids in North Sea surface sediments by absorption spectroscopy. Mar. Geol., 2000, 164: 173-181. www.elsevier.nl/locate/margo

[35] Niu, H.; Yang, H.; Tong, L.; Zhong, S.; Liu, Y. Spectral study of humic substance extract from pressurized oxidizing slag of Carlin-typed gold deposit. J. Phys.: Conf. Ser., 2019, 7: 1347-012027.

[36] Jangorzo, NS. Quantification du processus d'agrégation dans les Technosols. Thèse de Doctorat à l'Université de Lorraine, Lorraine, France, 2013, 188 p.

[37] Guergazi, S.; Amimeur, D.; Achour, S. Elimination des substances humiques de deux eaux de surface algériennes par adsorption sur charbon actif et sur bentonite. LARHYSS J., 2013, 13: 125-137.

[38] Wang, M; Liao, L; Zhang, X; Li, Z. Adsorption of low concentration humic acid from water by palygorskite. Appl. Clay Sci., 2012, 67: 164-168. https://doi.org/10.1016/j.clay.2011.09.012

[39] Ahangar, A. G. The effect of minerals on non-ionic compound sorption by changing the sorption capacity of soil organic matter. J. Soil Sci. Plant Nutrition, 2012, 12(4), 825-833.

[40] Blacke, G. U.; Kulikova, N. A.; Hesse, S. Adsorption of humic substances onto kaolin clay related to their structural features. Soil Sci. Soc. Am. J., 2002, 66: 1805-1812.

[41] Kleber, M.; Eusterhues, K.; Keiluweitk, M.; Mikutta, C.; Mikutta, R.; Nico, PS. Mineral–Organic Associations: Formation, Properties, and Relevance in Soil Environments. Adv. Agron., Elsevier Inc., 2015, 130: 0065-2113.

[42] Sigg, L. Regulation of trace éléments in lakes: the role of sedimentation. In: J. Buffle, and R. R. De Vitre Eds., Chem. Biol. regulation aquatic systems, Lewis, 1994, 175-195.

[43] Coulibaly. S. L. (2014). Abattement des phosphates des eaux usées par adsorption sur des géo-matériaux constitués de Latérite, grès et schistes ardoisiers. Thèse de Doctorat, Université de Lorraine, (France)/Université NANGUI ABROGOUA, Abidjan, Côte d'Ivoire, 233 p.

[44] Daifullah, AAM; Girgis, BS.; Gad, HMH. A study of the factors affecting the removal of humic acid by activated carbon prepared from biomass material. Colloids Surf. A., 2004, 235: 1-10.

[45] Chotzen, R. A.; Polubesova, T.; Chefetz, B.; Mishael, Y. G. Adsorption Of Soil-Derived Humic Acid By Seven Clay Minerals: A Systematic Study. Clays and Clay Minerals, 2016, 64, 628-638.

[46] Salman, M.; El–Eswed, B.; Khalili, F. Adsorption of humic acid on bentonite. Applied Clay Sci., 2007, 38: 51-56.

[47] Zhang, L.; Luo, L.; Zhang, S. Integrated investigations on the adsorption mechanisms of fulvic and humic acids on three clay minerals. Colloids Surf. A., 2012, 406: 84-90. https://doi.org/10.1016/j.colsurfa.2012.05.003

[48] Koua-Koffi, N. A. A.; Coulibaly, L. S.; Sangare, D.; Coulibaly, L. Laterite, sandstone and shale as adsorbents for the removal of arsenic from water. Am. J. Analyt. Chem., 2018, 9: 340-352.

[49] Achour, S. et Seghairi, N. Possibilités de rétention de substances humiques par adsorption sur la bentonite. LARHYSS J., 2002, 01: 08-14.

[50] Gueu, S. Elimination des acides humiques presents dans l'eau par adsorption et/ou photocatalyse. Thèse de Doctorat, Université de Lorraine, (France)/ l'Institut National Polytechnique Felix Houphouet Boigny de Yamoussoukro, Yamoussoukro, Côte d'Ivoire. 2019, 136 p.

https://cea-valopro.inphb.ci/uploads/publications/publication %20these/umri%2058/GUEU%20Soumahoro.pdf

[51] Zhang, Y. Y.; Lv, J. W.; Song, Y.; Dong, X. J.; Fang, Q. Study on kinetics of adsorption of humic acid modified by ferric chloride on U(VI). Earth and Environ. Sci., 2017, 94: 012-185. https://doi.org/10.1088/1755-1315/94/1/012185

[52] Abdel-Rahman, L. H.; Abu-Dief, A. M.; Al-Farhan, B. S.; Yousef, D et El-Sayed, M E A. Kinetic study of humic acid adsorption onto smectite: The role of individual and blend background electrolyte. AIMS Materials Sci., 2019, 6(6): 1176-1190.