Synthesis of an inorgano-clay complex from Loukolela clay and application in the adsorption of humic matter

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Abstract

To study the possibility of improving the ability to eliminate humic organic matter in water was the main focus of this work. For this, the objects of study were the fine fraction and the raw clay. Extraction of the fine fraction was carried out by the sedimentation technique either with prior treatment with oxalic acid to remove the iron oxides or without treatment. The particle size distribution of fine fraction obtained was achieved using laser granulometer. The adsorption capacity is determined using spectrophotometric measurements. The adsorption kinetics gave a necessary contact time to reach the equilibrium of 5 hours with the raw clay and 2h30min for the fraction fine with high removal efficiencies. The fine fraction was firstly made sodium and then the intercalation of an iron-based polycation in montmorillonite was carried out. Adsorption isotherms were obtained on the raw clay, the clay rendered sodic and on the intercalated clay. Isotherms modeling used the Langmuir and Freundlich models. The correlation coefficients indicated that these models are in good agreement. The maximum adsorbed quantities according to the Langmuir model indicate a considerable increase of the specific surface area in the intercalated clay, greatly improving the removal efficiencies of the organic matter. The parameter 1 / n allowed to consider that the adsorption is not favorable with the raw clay, whereas it is considered in the case of the intercalated clay.

Keywords: Clay, adsorption, humic substance, intercalation, inorgano-clay complex, Langmuir, Freundlich.

Introduction

Chlorination appears to be the least expensive and most widely used process worldwide[1]. Chlorine is one of the most important oxidants used for the chemical disinfection of drinking water because it is effective. However, aside from its biocidal action, it combines with the organic matter of natural waters. This can consume strongly the introduced chlorine thus limiting its disinfecting role and can lead by this reactivity to the formation of potentially toxic organohalogen compounds[2,3] particularly trihalomethanes[4,5]. High organic contents in water are generally found in lakes and rivers (surface water) and in shallow, poorly constructed wells whose waters can be contaminated by surface water Surface waters (Djoué and Djiri rivers) are the main sources of supply for the national water supply company (SNDE) in Brazzaville locality (Congo). And these rivers are in contact with heavily wooded areas and crossing residential areas and thus becoming "trash" especially for the Djoué river. Assuming that the treatment with chlorinated products could lead to the presence of trihalomethanes in the water distributed by the SNDE, it is therefore interesting to look for processes to eliminate as much organic matter as possible in the water collected. While filtration and flocculation-coagulation with aluminum sulphate can significantly reduce organic matter, the addition of sorbent treatment will optimize the removal of

organic matter. Numerous studies on the removal of organic matter by clays and in particular clay soils containing smectites are reported in the literature[6-8]. Raw clays have a generally low adsorption capacity that is often improved by: i. Thermal and / or acid activation[9,10,] ii. Intercalation of molecules in the interfoliar space[11,12].

This work aims to optimize the use of Loukolela clay which has been found to contain smectites in the removal of organic matter. Specifically, we will first study adsorption on the raw material (adsorption kinetics, adsorption isotherm, modeling of adsorption). In a second time we will consider studying the adsorption on the fine fraction. Finally we will modify the clay by intercalation of an iron polymer.

Material and methods

Material: The clay used in this work was taken in the locality of Loukoléla. The dominant clay species is montorillonite. There are also kaolinite and quartz[13].

Reagents used: Sigma Aldrich brand sodium humate has been used to prepare the different solutions of organic matter.

Extraction of the fine fraction: the clay deposits contain impurities at varying levels that alter the properties of clays.

Extraction of the fine fraction (<2μm) helps to remove impurities. It was done by the sedimentation technique by stabilizing the suspension with sodium hexametaphosphate. The extraction of the fine fraction was carried out either by treating the sample beforehand with oxalic acid in order to eliminate the iron oxides[14] or without treating the sample. 40g of sample are suspended in a solution of sodium hexametaphosphate for 24 hours. The suspension is homogenized using an electric homogenizer for 3 minutes. It is kept at room temperature and placed in a 2000ml test tube. After stirring the suspension at a time t = 0 min, the suspension sediments according to the law of Stokes. At t = 1h 35min, using a pipette, the fraction less than 2μm is taken from a depth of 2cm and for this purpose, the sampling operation is carried out several times. Several washing is carried out with distilled water of this fraction and then dried in an oven at 105°C. The montmorillonite samples are rendered homoionic sodium (Louk-Na) by five successive treatments with a solution of sodium chloride NaCl (1M). This operation is followed by several successive washes with distilled water.

Granulometry measurement by a laser granulometer: Laser diffraction granulometry was used to control the size distribution and determine the degree of quartz removal. The laser diffraction particle size analysis was carried out at the Center for Transfer of Ceramic Technologies (CTTC) in Limoges (France). The grain size distribution was determined using a HORIBA Partica LA-960 laser diffraction granulometer in a range of analysis ranging from 0.04 to 2000μm. The size distribution of the particles was obtained after suspension in an aqueous solution of sodium hexametaphosphate (HMP) concentration 0.1% by weight. The suspension was shaken under ultrasound for 10 min before the results were acquired.

Preparation of the iron-based polycation solution (PCBF): The iron-based polycation is prepared by basic hydrolysis from the 0.43M iron nitrate solution ($Fe(NO_3)_3.9H_2O$) and a 0.75M sodium hydroxide solution (NaOH). The addition of the NaOH solution is carried out with a batch rate of 0,6mL.mn^{-1}. The prepared "PCBF" solution is put in a dark bottle. During the addition, the homogenization of the sodium hydroxide solution and of the iron nitrate is carried out with stirring using a magnetic stirrer until the formation of the precipitate of the $Fe(OH)_3$ metal hydroxide. This solution is kept for 10 days for maturation. Intercalation of iron-based polycation in clay: The purpose of intercalation of metal polycations in sodium homoionic montmorillonite (Louk-Na) is not only to space the mineral layers as far as possible and to further enlarge their basal distances, but also, create pores in this mineral. The intercalation of polycations in montmorillonites is carried out according to a classical procedure[12]. 5g of Louk-Na are dispersed in 50ml of distilled water. The suspension is stirred for 1hour. A solution of PCBF contained in the burette is added dropwise (8.1ml min-1) to the clay suspension maintained with rapid stirring. The mixture is allowed to settle for 4 hours in order to ensure insertion. After 3 washes by centrifugation with

distilled water, the pellet is recovered and dried in an oven at 40°C for 24 hours. The inorgano-montmorillonite complex is thus obtained.

Measurement of adsorption power by spectrophotometry: The adsorption capacity of clays is determined by the difference in optical densities of the sodium humate solution before and after reaction with either the raw clay or the sodium clay again with the intercalated clay. Optical density measurements are made using a ZUZI model 4211/50 spectrophotometer. The wavelength used is 300nm. Quartz vessels of 1cm optical path are used. The solvent being distilled water; control samples without adsorbent are prepared to verify that there is no interference over time.

Sodium humate adsorption kinetics on clay: The kinetics of adsorption is realized on the sodium humate solution of initial concentration of 40mg/l. 25ml of the solution of humate are sampled and put in contact with a mass of 0.1g of Louk-B or modified. The suspensions are stirred at different times and then centrifuged. The optical densities of the supernatants are measured using a ZUZI spectrophotometer. The concentrations of sodium humate at equilibrium after different contact times are deduced as well as adsorbed amounts of sodium humate. Then the curves of the adsorbed amounts of sodium humate as a function of contact time are plotted.

Adsorption isotherms of sodium humate: The stock solution of sodium humate (1000mg/L) was prepared by dissolving 0.1g in 100ml of distilled water. The daughter solutions to be used for the analysis were obtained by successive dilutions of the stock solution (5; 15; 25; 30; 40mg/L). The experiments are carried out in 50ml Erlenmeyer flasks at room temperature. A mass of 0.1g of the sample is added to 25ml of the daughter solution of sodium humate (100mg/l). The mixtures obtained are stirred with a speed of 800rpm. These experiments are carried out with different times obtained by the kinetics of each of the samples (raw and sodium). At the end of each experiment the liquid and solid phases are separated by centrifugation for 10min at 3000rpm. The solutions obtained are analyzed by UV-Visible spectrophotometry.

The amount of adsorbed humic substances at equilibrium, q_e(mg/g) was calculated[15].

$$q_e = \frac{(c_o - c_e)v}{w} \tag{1}$$

c_o initial concentration of humic substances (mg/L), c_e equilibrium concentration of humic substances (mg/L), V volume of solution (L), W mass of dry adsorbent used (g)

Results and discussion

Raw clay adsorption: Kinetics of adsorption: The adsorption kinetics was first performed on the raw clay to determine the time required to reach equilibrium. Figure-1 gives us the removal percentage of humic substance by the raw clay material as a function of the contact time.

The evolution of the humic substance elimination curve by raw clay can be decomposed into 2 phases: i. very fast first phase, which can be explained by the existence of easily accessible adsorption sites, ii. a second phase of medium speed, to reach the saturation plateau, which marks diffusion towards less accessible adsorption sites before reaching an adsorption equilibrium where all the sites become occupied.

The maximum adsorption is reached after 5 hours of contact, with an adsorption percentage of the order of 80%. Contact times of the order of a few hours in the adsorption of humic substances in synthetic solution of distilled water on bentonites were observed[16]. The chemical analysis of the Loukolela clay gives 0.47% CaO, which is consistent with the results of the XRD which gives a peak at 15 Å suggesting the presence of calcium montmorillonite[13]. This observation could explain an relatively high adsorbability of Loukolela raw clay. Indeed it was showed that humic substances form complexes with some metals (calcium, copper, etc.) and the presence of these on adsorbents increases their adsorbability[16].

Adsorption isotherms: The adsorption isotherm is obtained by plotting the curve of the adsorbed quantity of humic substance (HS) per mass unit of clay Qe (mg.g-1) as a function of the equilibrium concentration Ce (mg/L) of HS. Figure-2 gives the HS adsorption isotherm by Louk-B clay.

This isotherm presents two parts: i. A first part: the adsorbed quantities increase with a relatively high slope as a function of the increase of the initial concentration, therefore the equilibrium concentration. ii. A second part: the adsorbed quantities remain constant (maximal adsorbed quantity) despite the growth of the equilibrium concentration.

This behavior can be explained by the presence of a large number of high SH ions in solution, which implies a massive adsorption within the material thus causing an increase in the capacity of adsorption of Louk-B higher. The curve obtained is of the normal L Langmuir form[17], indicating the flat adsorption of bi-functional molecules. In fact, humic substances possess a great chemical polyfunctionality (esters, alcohol, carboxylic acid, phenolic function). The carboxylic and phenolic functions of humic substances have a fairly wide pKa distribution because of the interactions between sites[18]. In this case the adsorption of the solvent is low and that of the solute on the solid is in a single layer. It should be noted that the value of the amount of pollutant retained at equilibrium is calculated from the absorption spectrophotometric assays.

Improvement of the adsorption capacity by inorganic-clay synthesis: Extraction of the fine fraction: Figure-3 represents the particle size distribution of the fine fraction obtained after a preliminary treatment and air-dried in the open air.

Figure-1: elimination efficiency of humic substances on raw clay as function of time.
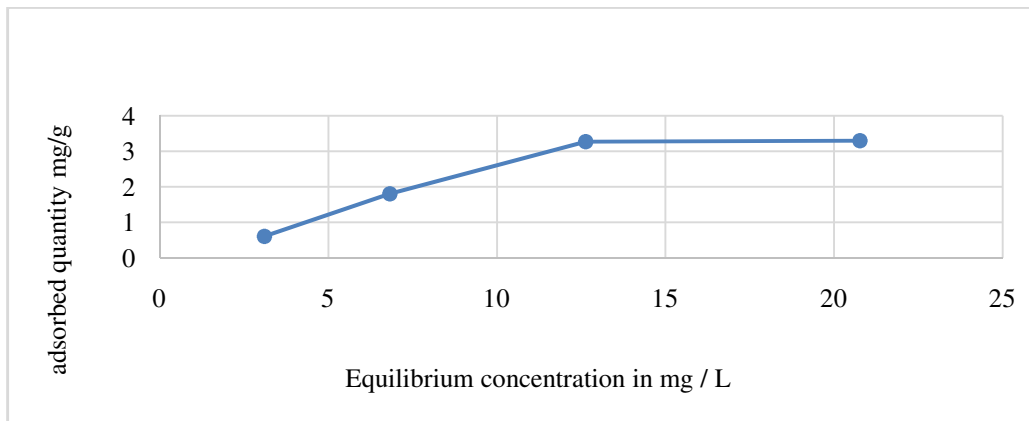

Figure-2: Adsorption isotherm of sodium humate by raw clay.

The frequency curve of fine fraction obtained with treatment spreads mainly in a monomodal way between 0.4 and 15 microns with however a coarser population but very minority is less than 1% of the population between 35 and 75 microns approximately. The mode of this distribution, ie the average diameter of the class of the most frequent particles corresponding therefore to the maximum of the frequency curve and to the point of inflection of the cumulative curve is equal to 2.47µm. . The median coinciding with the mode, the coarse fraction and the fine fraction are symmetrical. In our case, the fraction less than 2.47µm is identical to the fraction greater than 2.47µm. Since the clay fraction is defined as the fraction smaller than 2µm, we can estimate that the silty fraction is relatively important in the extract obtained after treatment of the raw sample. Indeed, clays generally comprise a particle size fraction between 2 and 20µm which is said to be a coarse clay fraction and may comprise sand, silt)[19]. The value of D10 (1.18µm) indicates that only 10% of particles have diameters less than 1.18µm and 90% of the particles would be a mixture of clay and loam particles (D90 = 5.15µm). In this extract, the presence although very small particles of dimensions ranging from 35µm to 75µm so sandy particles (> 20 microns) on the one hand and the other relatively large presence of the silty fraction lead to consider that the separation of the clay fraction was not effective. On the X-spectrum of Louk-B, we notice the presence of lines related to quartz. The good crystallinity of the quartz vis-à-vis the clay minerals justifies the fairly high height of quartz lines. This does not correspond to an abundance of quartz.

Figure-4 shows the particle size distribution of the untreated and air-dried Louk-B powder.

The frequency curve of the ntreated sample spreads monomodally between 0.3 and 2 µm. The following particle size indices were determined from this frequency curve; i. D10 = 0.52, ii. D50 = 0.79, iii. D90 = 1.18.

50% of the particles (D50) have a dimension less than 0.79 and 90% of the particles with dimensions smaller than 1.18µm. Many observations made on several clay minerals clearly indicate that kaolinites and illites have larger particles than montmorillonites[20]. With 50% of particles lower than 0,79µm, we can afford to consider an abundance of smectites. In any case, the maximum dimension in this extract is 2 µm. We are led to consider that the clay fraction is present in this extract.

Kinetics of adsorption of the fine fraction: We used the extract without treatment. Figure-5 gives us the variation of the adsorbed quantities of humic substance with the fine fraction of Louk as a function of the contact time.
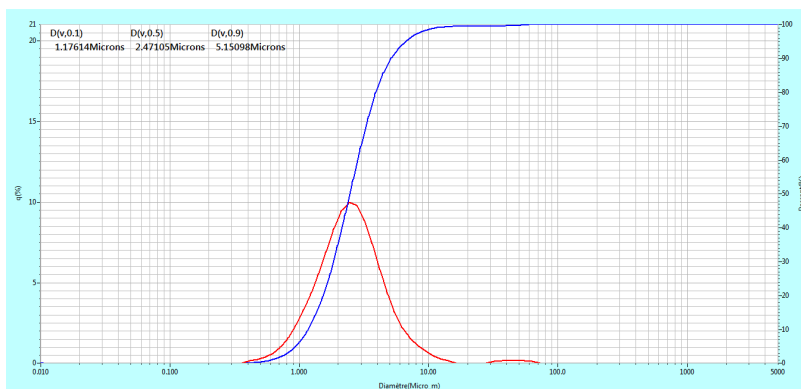

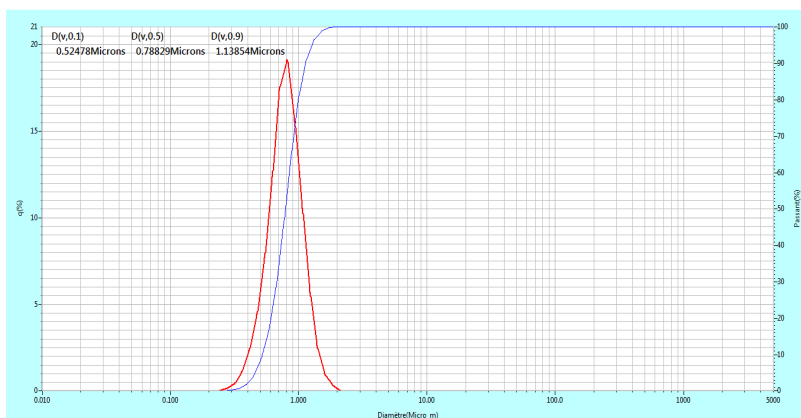**Figure-3:** Particle size distribution of the fine fraction with treatment.

Figure-4: Particle size distribution of the fine fraction without treatment.

The curve is divided into three parts: i. A first part ranging from 0 minutes to 60 minutes: the adsorption rate is very low (slow phase), ii. From 60 minutes to 100 minutes, an high increase of the rate of adsorption is observed, iii. From 100 minutes, the rate of adsorption becomes very low and reaches a constant value (equilibrium time).

Equilibrium is achieved in a shorter time compared to the case of raw clay (150 minutes). Indeed the fine fraction has a greater affinity. Indeed, the raw clay has a particle size distribution more spread and coarser than that of the fine fraction and also this fine fraction contains more particles capable of adsorbing a large number of substances.

Adsorption isotherms: Figures-6 and 7 give us respectively the adsorption isotherms of sodium humate by montmorillonite sodium and by intercalated montmorillonite.
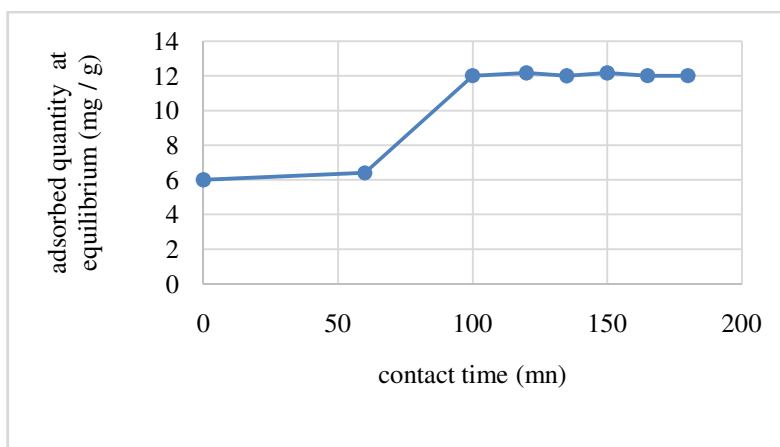

Figure-5: Evolution of adsorbed quantities of sodium humate at equilibrium on fine fraction of Loukolela clay as function of contact time.
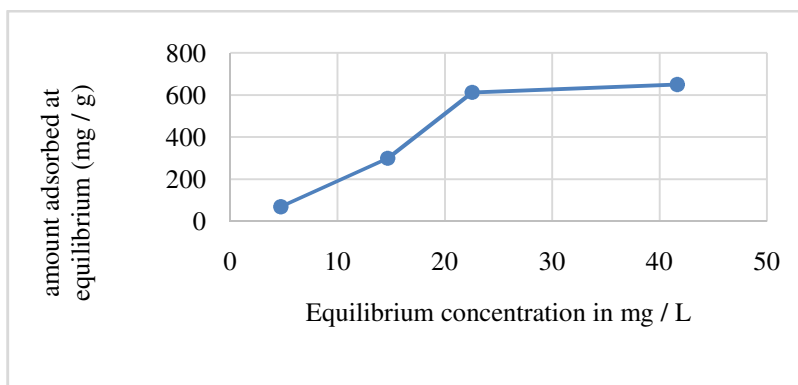
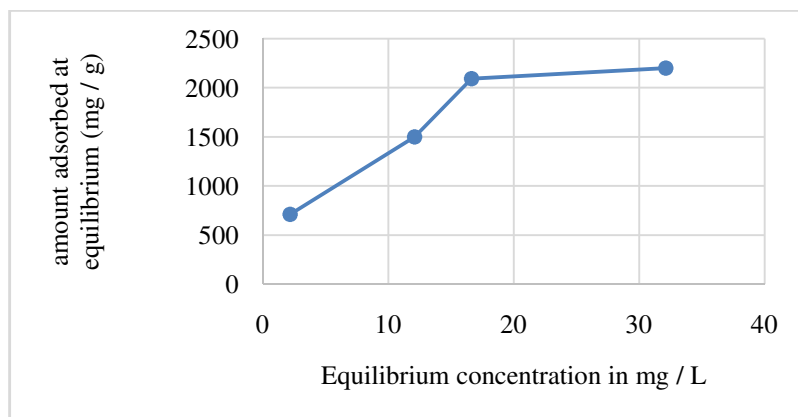

Figure-6: Adsorption isotherm on Na-clay.

Figure-7: Adsorption isothern on intercalated clay.

The adsorption isotherms have the same appearance as that of the raw clay. Maximum adsorbed amounts increase for Na clay (650mg/g) and intercalated clay (2200mg/g) relative to the raw clay. If the raw clay still contains non-reactive materials (quartz) reducing its adsorption capacity, the extraction of the fine fraction and therefore the concentration of the clay fraction explains the increase of the adsorption capacity in the clay-Na and intercalated clay.

The adsorption capacity of the intercalated clay is 3 times greater than that of the Na-clay. This fact reveals that the intercalation of the iron-based polycation has increased the adsorption sites. The curves corresponding to adsorbed quantities as function of equilibrium concentration can be classified L type according to classification of Giles and coll[17].

Modelization of adsorption isotherms: Two widely used models in the literature have been chosen: the Freundlich model (which is a potential law), the Langmuir model (based, among other things, on the hypothesis of a monolayer on the surface).

Application to the LANGMUIR model: The Langmuir model is based on the assumption that adsorption takes place at specific homogeneous locations in the adsorbent.

The Langmuir linear equation is: $\frac{1}{q_e} = f(\frac{1}{C_e})$ (2)

The figures give us the plots of linearized Langmuir equations relating respectively to the adsorption isotherms on raw clay (Louk B), Na-clay (Louk Na) and intercalated clay (Louk Fe)
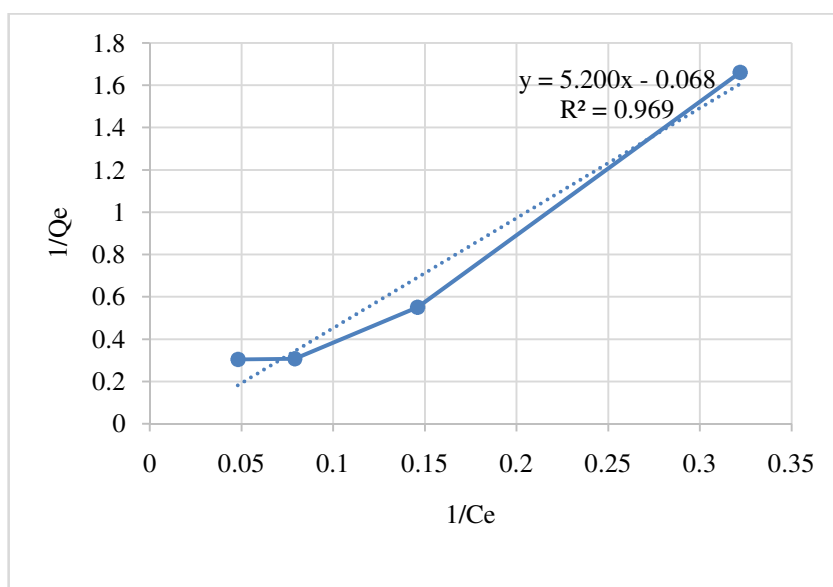

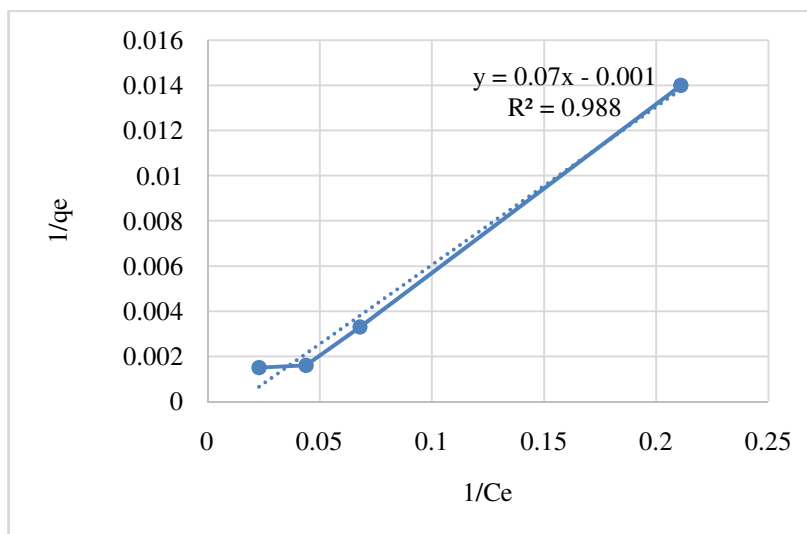**Figure-8:** Langmuir adsorption isothern for raw clay.

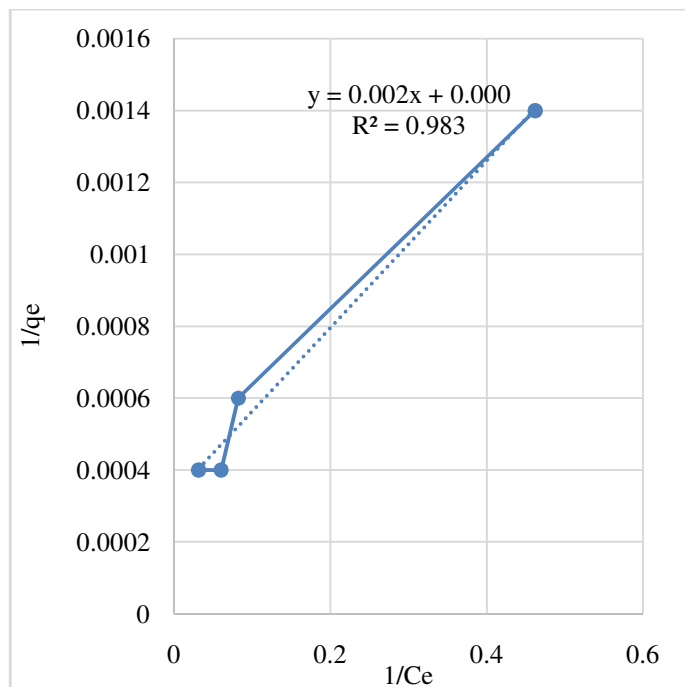**Figure-9:** Langmuir adsorption isothern for Na-clay.

Figure-10: Langmuir adsorption isothern for intercalated clay.

From these equations the Langmuir parameters have been deduced and recorded in the table.

Table- : Langmuir parameters

Paramètre	q_m (mg/g)	K_L (L/mg)	R^2
Louk B	7,33	0,028	0,969
Louk Na	524,7	0,033	0,988
Louk Fe	1962,45	0,26	0,983

The maximal adsorption capacity q_m increases from raw clay to Louk Na and more strongly to Louk Fe. The extraction of the fine fraction allowed enrichment of clay species thus increasing the concentration of the adsorbent species. The very strong growth of the maximum adsorption capacity on Louk Fe, taking into account the Langmuir hypothesis, implies an increase in the specific surface area during intercalation. The very low values of K_L parameter related to the ratio of adsorption and desorption rates would indicate a relatively low affinity of humate with Louk B and Louk Na. This affinity increases at the level of Loik Fe as K_L in Louk Fe is practically multiplied by 10 compared to Louk B and Louk-Na. The correlation coefficients show that the adsorption equilibria of these systems are suitably described by the Langmuir models.

Application to the Freundlich model: The figures give us the linearized equations in the Freundlich model.
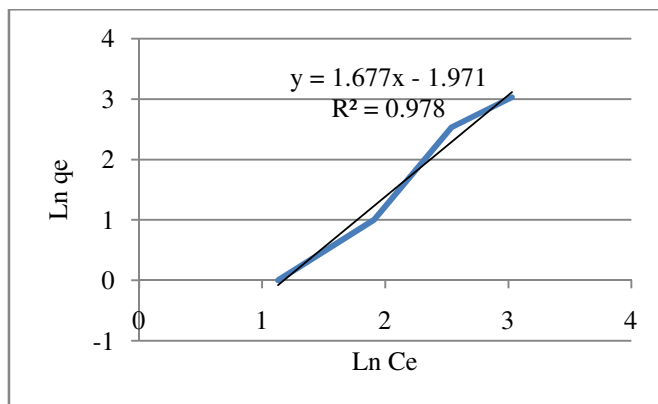

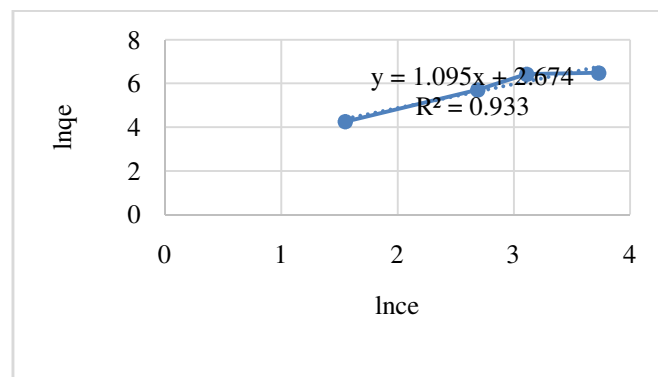**Figure-11:** Freundlich adsorption isothern for raw clay.

Figure-12: Freundlich adsorption isothern for Louk-Na.
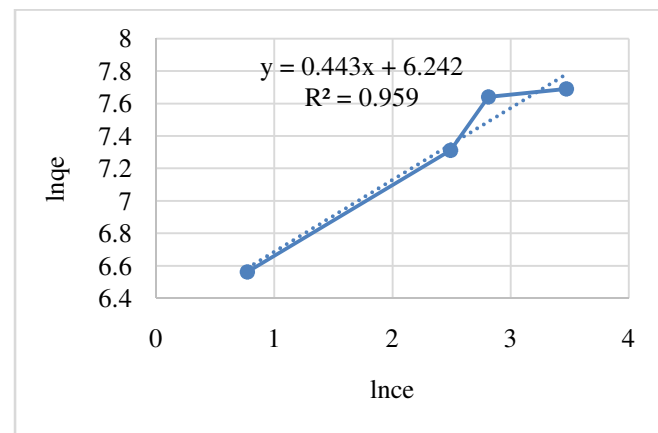

Figure-13: Freundlich adsorption isothern for Louk-Fe.

The resulting Freundlich parameters are collated in the table.

Table- : Freundlich parameters

	1/n	K_F	R^2
Louk B	1,677	0,14	0,978
Louk Na	1,095	14,49	0,933
Louk Fe	0,443	2,691	0,959

In Louk B, 1/n being greater than 1, the adsorption is not favorable, the adsorption bonds are weak and the adsorption capacity decreases. In Louk Na the parameter 1/n is approximately equal to 1, the adsorption is linear, the sites are then homogeneous and there are no interactions between the adsorbed species. In Louk Fe with 1/n less than 1, the adsorption is favorable, the adsorption capacity increases and new adsorption sites appear. The correlation coefficients show the Freundlich model agrees with the adsorption equilibria.

Conclusion

The objective of this work was to study the possibility of improving the ability to eliminate humic organic matter in water. For this, the studies were carried out on the raw clay and on the fine fraction. Extraction of the fine fraction was carried out by the sedimentation technique either with prior treatment with oxalic acid to remove the iron oxides or without treatment. The laser particle size determined the best fine fraction. The adsorption kinetics gave a necessary contact time to reach the equilibrium of 5 hours in the case of the raw clay and 2h30min in the case of the fraction. Fine with high removal efficiencies. The fine fraction was made sodium and the intercalation of an iron-based polycation in montmorillonite was carried out. Adsorption isotherms were obtained on the raw clay, the clay rendered sodic and on the intercalated clay. Isothermal modeling used the Langmuir and Freundlich models. The correlation coefficients indicated that these models are in good agreement. The maximum adsorption capacities determined in the Langmuir model indicate a considerable increase in the specific surface area in the intercalated clay, greatly improving the removal efficiencies of the organic matter. The parameter 1 / n allowed considering that the adsorption is not favorable with the raw clay, whereas it is considered in the case of the intercalated clay.

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