

## Adsorption Tests of Humic Substances on Raw Clay from Bikougou (Gabon)

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### Abstract

The presence of organic material of natural origin is characteristic of surface waters. Humic substances (HS) are generally the largest category in these waters. The objective of this work was to evaluate the adsorption performance of raw clay from Bikougou (Gabon) for the removal of humic substances.

During the experimental study, the batch equilibration technique was used to follow the kinetics of adsorption of humic substances on clay. The influence of reaction parameters such as the initial concentration, the pH of the solution and the presence of inorganic salts (calcium or magnesium ions) was also observed. Optimum removal is obtained for low values of initial concentrations. pH variation showed that acidic medium (pH 4) can achieve good yields retention of humic substances. The presence or absence of mineral salts in the medium appears as one of the most critical parameters. Indeed, the impact of water mineralization has resulted in a significant improvement in removal efficiency of humic substances, taking as reference the results obtained in demineralized water. The promoting effect of cations such as calcium and magnesium may be the cause of this improvement. This let suggest a mechanism based on adsorption bridging clay-cation-SH. The kinetic study also showed that the adsorption equilibrium is reached after more than ten hours of reaction, whatever the dilution medium humic substances.

**Keywords:** Clay, adsorption, humic substances

### I. Introduction

Surface waters that feed the production of drinking water contain, different concentrations of organic compounds including a significant amount of humic substances (HS). Humic substances in surface water causes a lot of problems such as colour, taste, odour and lower efficiency in water treatment process (Niemeyer *et al.*, 1992 ; Yu & Jiang, 2010). In the field of natural organic matter, humic substances mainly composed of humic and fulvic acids are a very large part.

The formation of humic substances remains one of the least understood aspects of the chemistry of humus. Several theories coexist on the origin of humic substances by plant involving the degradation of lignified tissues and microbial origin by the decomposition of other organic residues (Flaig, 1988; Lichtfouse *et al.*, 1998 ; Eyheraguibel, 2004 ; Labanowski, 2004). Humic substances have no homogeneous, exactly specified, chemical composition (Schulten & Leinweber, 1996; Francou, 2003 ; Peña-medez *et al.*, 2005). By their organic nature, the major components of humic substances are carbon and oxygen. There are also hydrogen, nitrogen, sulfur etc.. (Koriko, 2010). HS have a large number of hydrophilic functional groups: carboxyl (COOH), phenolic and / or alcoholic (OH), carbonyl (C = O) and amine groups (NH<sub>2</sub>). OH and COOH groups give typical properties of HS. The proportion of COOH groups is often greater than 50% (Citeau, 2004).

In the preparation of drinking water, the humic substances as well as residues from the reagents used for the treatment of the water must be removed. Their presence should always be considered especially if the water must be disinfected with chlorine. Indeed, this can lead to high chlorine consumption accompanied by the formation of organohalogen products that cannot be removed by conventional treatment processes (Chow & Robert, 1981). These organochlorines are a risk of long-term toxicity (mutagenic and / or carcinogenic) (Croue, 1987; Le Curieux *et al.*, 1996 ; Achour & Guergazi, 2002).

Among techniques used for the removal of humic substances, coagulation, adsorption and membrane processes are widely adapted. However, adsorption has gained increased credibility during recent years, as it offers a technically feasible and economical approach (Ayele *et al.*, 1990 ; Jaruwong & Wibulswas, 2003 , Yu & Jiang,

**2010**). Adsorption of humic substances on clay minerals has been of interest to many researchers (**Seghairi et al, 2004 ; Wang & Xing, 2005**). The results are varied and are closely related to study conditions. The adsorbent used in this work is a clay from Bikougou (GABON), chosen for its high availability and especially for its adsorptive properties to fix heavy metals (**Eba et al., 2010 ; Eba et al., 2011**).

The objective of this study is to observe the retention capacity of the clay raw towards humic substances (HS). In order to improve the adsorption capacity, the influence of various parameters such as pH, reaction time and especially mineralization (adding calcium and magnesium ions) of the dilution medium was studied.

## II. Materials and methods

### II.1 Characteristics of clay

The clay used in this study comes from Bikougou (GABON). Its mineralogical and physico-chemical characteristics are presented in Tables 1 and 2, respectively (**Eba et al., 2012**).

### II.2 Extraction of humic substances:

Humic substances used in this study are extracted from compost plant debris. Compost is delipidated by treatment with a mixture of the solvent chloroform-methanol (2: 1), then the residues of the samples were evaporated to remove the remaining solvent (**Lichtfouse et al., 1998**). The compost is then treated 3 times with distilled water to get rid of non-humic substances soluble (sugars, proteins) that may interfere with humic substances (**Amir et al, 2003**). The extraction of humic substances is carried out using 1N sodium hydroxide; 50 g of compost in an Erlenmeyer flask, and adds 250 ml of 1N sodium hydroxide. The whole is thoroughly mixed and allowed to stand for 24 hours. The supernatant was filtered. The filtrate containing humic and fulvic acids, is measured as total organic carbon (TOC) method **Anne (1945)** and translated into mg/L of humic substances. This solution of known concentration served as HS stock solution.

### II.3. Description of the dilution medium

The HS stock solution was diluted in three different media: A first medium consisting of demineralized water, a second consisting of demineralized water fortified with calcium, a last consisting of demineralized water enriched magnesium only. The calcium and magnesium ions are respectively from calcium and magnesium sulfate.

### II.4 Adsorption studies

The adsorption experiments were carried out using the batch equilibration technique. In 50 mL of solutions of humic substances placed in Erlenmeyer flasks was added 0.5 g of clay. HS solutions have initial concentrations 50, 75 and 100 mg/L. The effect of pH on the adsorption was studied. For this, the pH of the solutions was adjusted to the values 4,0 ; 6,0 and 8,0. At the end of the predetermined time intervals, the solutions were filtered on filter papers 0.45 µm and analyzed by Spectrophotometer Spectronic 20D + Milton Roy, to determine their optical density. Using the calibration curve, the residual concentrations of humic substances are known. These calibration curves established for each dilution medium were obtained as follows: HS Solutions of different concentrations were prepared by serial dilutions of stock solution. Optical density values of these solutions were measured at 472 nm and plotted against the concentration values.

The adsorption rate was calculated as the following equation:

$$\% \text{ adsorption} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

With  $C_i$  and  $C_e$  (mg/L) are the initial and equilibrium concentration of HS.

The amount  $q_e$  (mg/g) of HS adsorbed was calculated based on the difference between the HS concentration in the solution before and after adsorption from relation:

$$q_e = \frac{(C_i - C_e) \cdot V}{m} \quad (2)$$

Where V (L) is the volume of HS solution and m (g) is the weight of the adsorbent.

### III. Results and Discussion

#### III.1. Effect of initial concentration

The effect of HS initial concentration on the adsorption by clay was investigated by varying HS concentration from 50 to 100 mg/L (Figure 1).

The results indicate an increase in the rate of adsorption while the initial concentration decreases and get a maximum retention of 40.2% for a level of 50 mg/L in HS. However, looking at the adsorption capacity of the adsorbent, the trend is reversed. In fact, the adsorption capacities of clay are 2.01, 2.55 and 2.8 mg/g for initial concentrations of HS 50, 75 and 100 mg/L, respectively. This latter observation is in agreement with the work done by **Amer et al. (2010)**. Improving the capacity of the clay could be explained by the fact that at high concentration, a significant number of adsorbable molecules are available.

#### III.2. Effect of pH

It is known that the adsorption is greatly influenced by the pH of the solution (**Singh et al., 1994 ; Jaruwong & Wibulswas, 2003 ; Djebbar et al., 2012**). To establish the effect of pH on the removal of HS by clay, the kinetic equilibrium has been carried out at different pH values 4, 6 and 8 (Figure 2).

It was observed that the lower is the pH, the greater is the humic substances removed. The retention rate was 32.8% at pH 8, while it is 50.8% at pH value 4. This can be explained by the fact that a change in pH causes a change in the ionic charge on the surface of the clay and also a change in the degree of ionization of HS **Achour & Seghairi (2002)**. This finding was consistent with that reported in the literature (**Schnitzer & Khan, 1972 ; Jaruwong & Wibulswas, 2003**). According to **Jaruwong & Wibulswas (2003)**, these observations might be explained by the following reasons. Humic substances are negatively charged in polyanion form and there is repulsion between humic substances and the natural negatively charged layer of the clays at high pH level. Conversely, at low pH level relatively few of the humic substances molecules are ionized and behave like uncharged molecules that can penetrate interlamellar spaces of the clay.

#### III.3. Adsorption kinetics

##### III.3.1. Equilibrium Time

The kinetics of adsorption of humic substances on clay was conducted for the three dilution media (Figure 3). The results showed that the equilibrium is obtained after at least ten (10) contact hours and that whatever the dilution medium.

Data from several adsorption kinetics of humic substances by various adsorbent show different equilibrium time. **Jaruwong & Wibulswas (2003)** in their study of the adsorption of SH reported that the equilibrium time is reached only after 20 minutes. **Achour & Seghairi (2002)** found that the equilibrium occurs after six hours, using clay from Algeria. **Ayele et al. (1990)**, for their study on the removal of humic substances by activated carbon have achieved a period of much greater saturation. Indeed, they found that equilibrium is reached after 24 hours.

##### III.3.2. Influence of dilution media

In order to evaluate the impact of dilution medium on the retention of SH, the study was conducted by diluting the SH in three different environments. One of the media is completely demineralised and the other two are either enriched in calcium or magnesium, respectively. The aim is to test the impact of mineral salts present in the water dilution of humic substances on the adsorption of the latter.

Significant differences (figure 3) were observed between the removal efficiency of humic substances diluted in demineralized solution (50.8%) and those related to humic substances diluted in medium enriched with minerals (65.3% for calcium and 73% for magnesium). The comparison of these results with those obtained in demineralized water lets say the presence of mineral ions in the dilution media directly affect the adsorption rate of humic substances on clay. The results indicated that addition of  $Ca^{2+}$  and  $Mg^{2+}$  improves obvious fixation of humic substances on clay. Positive ions ( $Ca^{2+}$  and  $Mg^{2+}$ ) are easily attracted to the surface of the clay. The entire

clay-cation can easily attach to molecules of humic substances and improve process efficiency consequently. **Achour & Seghairi (2002)** obtained similar results. According to them, the cations present in the dilution water serve as a bridge between the clay particles and SH, and the formation of complex adsorbent-adsorbate-cation would increase the rate of elimination. Also as illustrated by the results (Figure 3), the adsorption rate is greatest when the dilution solution is enriched with magnesium ions.

#### IV. Conclusion

The objective of this study was to examine the possibility of adsorption of humic substances on raw clay of Bikougou (Gabon). The tests were aimed to see the adsorptive properties of clay and secondly to improve the performance of this clay. For this purpose, the study were carried out on the influence of various parameters such as initial concentration of HS, the solution pH, contact time and especially mineralization of dilution medium.

The batch adsorption results clearly demonstrate the ability of the sorbent clays to remove humic substances from water. The variation of pH indicates that adsorption of humic substances was very sensitive to pH. The lower the pH, the greater the humic substances removed. The study also revealed that equilibrium is reached after ten hours of contact. The physico-chemical characteristics of the environment and mineralization appear to be particularly critical in optimizing the removal of HS on clay. Indeed, the addition of calcium or magnesium ions into HS solution enhances the adsorption affinity of the clay towards humic substances. The adsorption rate is maximum when the medium was enriched with magnesium ions 73% and 65.3% when the medium is enriched with calcium ions.

Further studies are needed to develop all these aspects and to determine optimal conditions for the use of clay in drinking water production.

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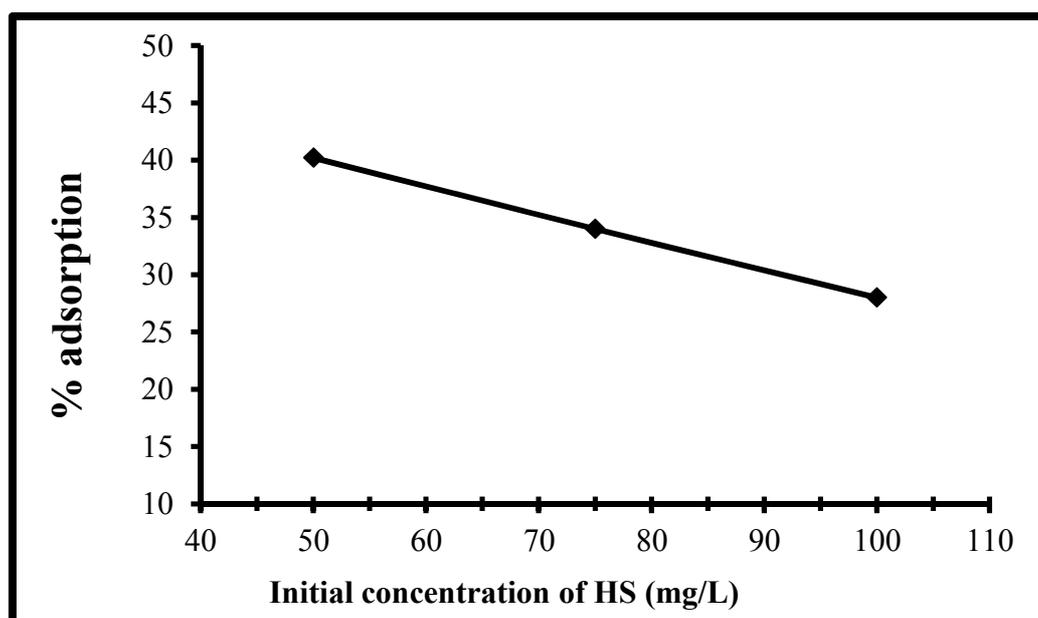
**Table 1:** Mineralogical characteristics of Bikougou clay (Eba et al., 2012).

Mineral	Raw clay (% wt)	Clay fraction (% wt)
Kaolinite	29.1	53.0
Albite	20.3	0.0
Montmorillonite	15.2	40.0
Illite	10.9	7.0
Quartz	19.1	0.0
Carbonate	3.0	0.0
Maghemite	1.2	0.0
Anatase	0.9	0.0

Ba-Sr hydroxyapatite	0.8	0.0
Zircon	Trace	0.0

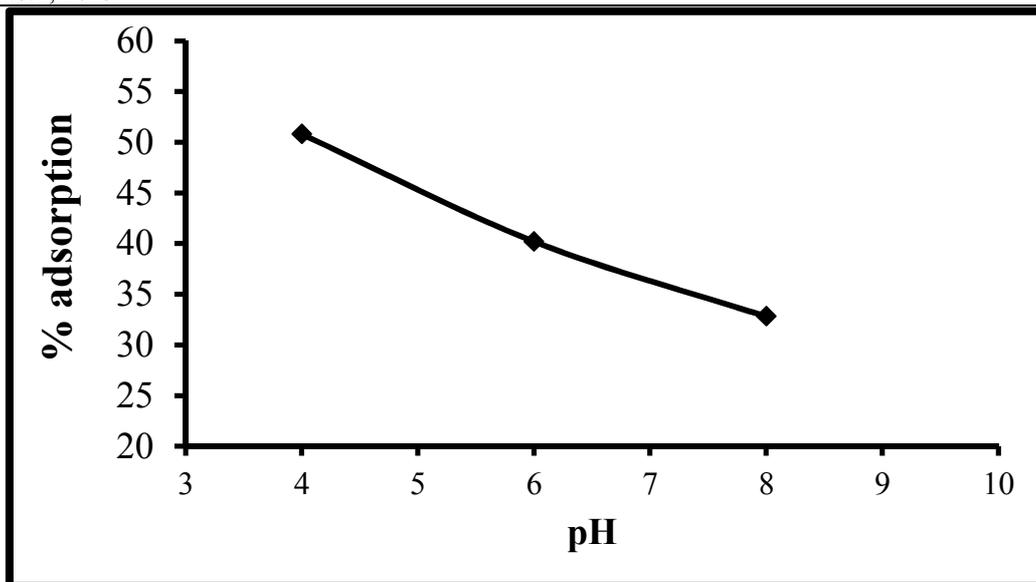
**Table 2:** Physico-chemical characteristics of Bikougou clay (Eba et al., 2012).

pH <sub>ZPC</sub>	CEC (meq/100g)	Acidity neutralizations (meq/g)			Surface area (m <sup>2</sup> /g)
		NaOH	NaHCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	
3	12,87	2,79	0,285	0	170



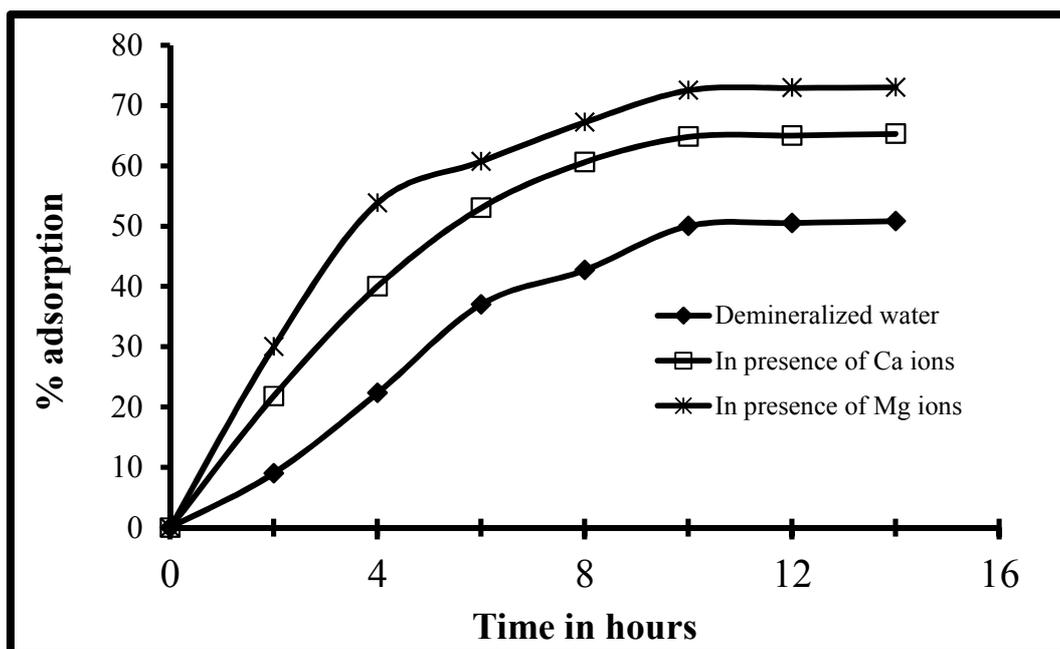
**Figure 1:** Variation of HS adsorption rate as a function of initial concentration.

Contact time: 14 hours; pH: 6; clay mass: 0,5g in 50 mL of HS solution; dilution medium: demineralized water.



**Figure 2:** Variation of HS adsorption rate as function of pH.

Contact time: 14 hours; initial concentration of HS: 50 mg/L; clay mass: 0,5g in 50 mL of HS solution; dilution medium: demineralized water.



**Figure 3:** Effect of contact time on HS adsorption in various dilution media.

Initial concentration of HS: 50 mg/L; pH: 4; clay mass: 0,5g in 50 mL of HS solution.

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