



## Study of the adsorption of Nickel ions on local natural clays in hydrometallurgical effluents

[Étude de l'adsorption des ions de Nickel sur des argiles naturelles locales dans les effluents hydrométallurgiques]

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### Abstract

This research focuses on the treatment of hydrometallurgical effluents, specifically studying the adsorption of metallic ions such as Nickel, Copper, Cobalt, Mercury, and lead on natural clays from the Democratic Republic of Congo (DRC). Twelve clay samples, six activated with a strong acid and six non-activated, were characterized using various techniques including X-Ray Diffraction, Fourier Transform Infrared Spectroscopy, X-Ray Fluorescence, Transmission Electron Microscopy, and chemical dosage. The characterization revealed that the clays are mixed with several clayey minerals, enriched in aluminum silicate; contain absorption and water retention sites, and exhibit heterogeneities at the interfaces between grains and exchangeable ions. Activating the clays increased their cation exchange capacities, removed impurities, and increased pore size and specific area. Two aqueous solutions were used in the experiments: a laboratory-prepared nickel sulfate solution and a hydrometallurgical aqueous solution from a factory, both initially containing 15 mgL<sup>-1</sup> of Ni<sup>2+</sup> ions. Results showed that the adsorption of Ni<sup>2+</sup> ions increased with the quantity of clay in the solution. The activated clays adsorbed more ions than non-activated clays at the same Ni<sup>2+</sup> ion concentration. Additionally, adsorption was weaker in the hydrometallurgical solution compared to the nickel sulfate solution, suggesting competition from other metallic ions. The optimal adsorption occurred with chemically activated clays containing high Na<sup>+</sup>, Fe<sup>2+</sup>, and Al<sup>3+</sup> ion content and low K<sup>+</sup> ion content. The Hill-Langmuir model was used to describe the adsorption results, revealing that minimal quantities of activated clay were needed to adsorb a large quantity of Ni<sup>2+</sup> ions in the solution, whereas large quantities of non-activated clays were insufficient. In conclusion, the research demonstrates the potential of natural clays from the DRC to adsorb metallic ions from hydrometallurgical effluents, providing insights for effective treatment methods in the future. The model revealed that the clay samples A2a clay, A6a and A3na have the very elevated reactional sites concentrations.

Keywords: Hydrométallurgiques effluents, adsorption of the ions, activation of the clays, Hill-Langmuir model

### Résumé

Cette recherche se concentre sur le traitement des effluents hydrométallurgiques, en étudiant spécifiquement l'adsorption d'ions métalliques tels que le nickel, le cuivre, le cobalt, le mercure et le plomb sur des argiles naturelles de la République démocratique du Congo (RDC). Douze échantillons d'argile, dont six activés avec un acide fort et six non activés, ont été caractérisés à l'aide de diverses techniques, notamment la diffraction des rayons X, la spectroscopie infrarouge à transformée de Fourier, la fluorescence des rayons X, la microscopie électronique à transmission et un dosage chimique.

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La caractérisation a révélé que les argiles sont mélangées à plusieurs minéraux argileux, enrichies en silicate d'aluminium ; contiennent des sites d'absorption et de rétention d'eau, et présentent des hétérogénéités aux interfaces entre les grains et les ions échangeables. L'activation des argiles a augmenté leurs capacités d'échange cationique, éliminé les impuretés, et augmenté la taille des pores et la surface spécifique. Deux solutions aqueuses ont été utilisées dans les expériences : une solution de sulfate de nickel préparée en laboratoire et une solution aqueuse hydrométallurgique provenant d'une usine, toutes deux contenant initialement  $15 \text{ mgL}^{-1}$  d'ions  $\text{Ni}^{2+}$ . Les résultats ont montré que l'adsorption des ions  $\text{Ni}^{2+}$  augmentait avec la quantité d'argile dans la solution. Les argiles activées ont adsorbé plus d'ions que les argiles non activées à la même concentration en ions  $\text{Ni}^{2+}$ . De plus, l'adsorption était plus faible dans la solution hydrométallurgique que dans la solution de sulfate de nickel, suggérant une compétition avec d'autres ions métalliques. L'adsorption optimale s'est produite avec des argiles activées chimiquement contenant une forte teneur en ions  $\text{Na}^+$ ,  $\text{Fe}^{2+}$  et  $\text{Al}^{3+}$  et une faible teneur en ions  $\text{K}^+$ . Le modèle de Hill-Langmuir a été utilisé pour décrire les résultats de l'adsorption, révélant que des quantités minimales d'argile activée étaient nécessaires pour adsorber une grande quantité d'ions  $\text{Ni}^{2+}$  dans la solution, alors que de grandes quantités d'argiles non activées étaient insuffisantes. En conclusion, la recherche démontre le potentiel des argiles naturelles de la RDC à adsorber les ions métalliques des effluents hydrométallurgiques, fournissant des perspectives pour des méthodes de traitement efficaces à l'avenir. Le modèle a révélé que les échantillons d'argile A2a, A6a et A3na présentent des concentrations de sites réactionnels très élevées.

Mots-clés : Effluents hydrométallurgiques, adsorption des ions, activation des argiles, modèle de Hill-Langmuir

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## 1. Introduction

The activities of mining extraction generate hydrometallurgical effluents loaded of metallic ions to variable concentrations. These effluents are sometimes rejected in the nature without any suitable treatment. The risk of pollution of water and the environment causes a big concern of the scientific community. It is imperious to treat some hydrometallurgical effluents before their dismissal in the natural habitat.

The processus of treatment of the hydrometallurgical effluents aim to reduce the polluting load to a level judged acceptable for the environment. They use some methods as the adsorption, the precipitation, the electrolysis, etc. The adsorption implies some materials adsorbants in the process of treatment.

Adsorbants materials can be pulverized in an aqueous solution of hydrometallurgical effluents. This solution is filtered then to rid it of the pollutants kept in the fine particles of the adsorbants materials. Some adsorbants materials present themselves as membrane who is immerses in an aqueous solution of hydrometallurgical effluents. After some time of immersion, the membrane charged of the pollutants agglutinated to the surface is withdrawn from the aqueous solution.

Research on the natural adsorbants materials as the frost of silica, the chitine, the chitosane and the clayey materials, preoccupied good number of the researchers. The treatment of hydrometallurgical effluents using clayey materials, for example, constituted an important theme of research. The mechanisms by which the metallic ions set on an adsorbant make the more intervene often of the electrostatic interactions, the strengths of Van Der Waals, of the links covalentes etc. The groupings of the loaded adsorbants negatively as the groupings carboxyliques, hydroxyles and phosphoric, are known for adsorb the metallic ions.

Some authors observed that a quantity of clay pulverized in aqueous solution exchange of the ions with this solution (Elfil, 1995). Other authors (Bouras 2003 ; Bhattacharyya et al., 2006) put in evidence the ionic exchange phenomenon in the process of the treatment of waters contaminated by metallic ions. Bhattacharyya et al. (2006) used two natural clays (a kaolinite and a montmorillonite) to eliminate the ions of copper in water. A natural clay (the vermiculite) used to eliminate the ions of the copper, the ions of

lead and the ions of the cadmium. Ghorbel et al. (2009) used the bentonite, a clay of the family of the smectites to eliminate the ions of the chromium in an aqueous solution. The montmorillonite is used for the dépollution of waters contaminated by mercury. Bouras (2003) used the montmorillonite, for the dépollution of the aqueous solutions contaminated by the chlorobenzène. Gaombale (2004) used the clay for the storage of the radioactive garbage.

The works of these authors show that the natural clays can serve for the treatment of hydrometallurgical effluents. The objective of this work is to study the adsorption of the  $Ni^{2+}$  ions of hydrometallurgical effluents on natural clays harvested thru Kinshasa and towards Kongo-central in Democratic Republic of Congo. Otherwise, the Democratic Republic of Congo arrange many clayey material sites whose use could be considered in the purification of the environment. The metallic ions as the Nickel, the Copper, the Cobalt, the Mercury, etc., appear among the metallic ions to strong concentration in the hydrometallurgical effluents of mining extraction.

## 2. Materials and Methods

The methodology is at a time experimental, objective and systemic. It consists in observing the phenomenon of adsorption of the ions of nickel on clayey materials pulverized in an aqueous solution of hydrometallurgical effluents. It also consists in describing in an objective way and to modelise the phenomenon of adsorption observed. For that to make, the samples of clays have been characterized to determine their various physico-chemical properties.

### 2.1. Materials

The natural clay samples come from Kinshasa ( $4^{\circ}00'00''\text{South}$  ;  $21^{\circ}00'00''\text{East}$ ), de Boma ( $5^{\circ}50'55''\text{South}$  ;  $13^{\circ}03'22''\text{East}$ ) et de Kisantu ( $4^{\circ}36'54''\text{South}$  ;  $15^{\circ}06'16''\text{East}$ ) in Democratic Republic of Congo. These samples are presented in the table 1.

*Table 1. Presentation of the studied clays not activated*

Clay code	Sampling sites	Clay color
A1na	Kisantu	Yellow
A2na	Kisantu	Grey
A3na	Kisantu	Black
A4na	Kinshasa (Limete)	White
A5na	Kinshasa (N'djili)	White
A6na	Boma	Grey

These samples have been dried in a steamroom to the temperature of 50 °C during 48 h. They have been ground then, sifted then in fine particles of less 40 μm of diameter. The temperature of drying fixed to 50 °C had to not destroy or to modify the structure of the clays. For every type of clay sample, a quantity has been activated in a suitable way in order to influence more meaningfully on the phenomenon of adsorption. Twelve different samples have been gotten thus among which, six activated clays samples and six non activated clays samples.

The chemical activation of the clays has been achieved of the following manner: A powder of natural clay is pulverized in 200 mL an aqueous solution of hydrochloric acid of 0,99 M. The gotten mixture is agitated during 8 h while it is heated until the boiling point. After agitation and heating, one lets rest the mixture during some time. The deposit of clay is rinsed 5 time then in water, dried then in an oven during 24 h to the temperature of 50 °C. After drying, the clay is ground sifted then in fine particles with an estimated diameter unless 40 μm. We get the activated natural clay (A1a, A2a, A3a, A4a, A5a and A6a).

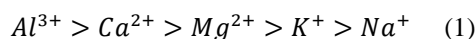
The clays samples have been characterized by : the X-Ray Diffraction (XRD), to study the crystalline structure and the mineralogical composition of the clays, the X-Ray Fluorescence (XRF) to identify and to quantify the present chemical elements in the clays; the Fourier Transform Infrared Spectroscopy (FTIR) to detect via the characteristic vibrations of the chemical links, the present chemical functions in the material; Transmission Electronic Microscopy (TEM) to study the surface morphology.

The chemical dosage has been used to determine the cation exchange capacity (CEC) of the clays. This technical consists in saturating the sites of ionic exchange of a material by the ammonium ions  $NH_4^+$  of the aqueous solution of ammonium acetate, to wash the material with the ethylic alcohol in order to eliminate the excess of the  $NH_4^+$  ions filling the sites others that those of exchange of ions. After washing with the ethylic alcohol, the material is pulverized then in an aqueous solution of *KCl*, an exchange results from it between *KCl* ions of the material and the  $K^+$  ions of the aqueous solution. The filtrate is kept and the deposit is pulverized again in another sample of the aqueous solution of *KCl*. The operation is repeated until *n* time in order to make

take all  $NH_4^+$  ions out of the material. The filtrates of the aqueous solution of *KCl* are united to determine the cation exchange capacity (CEC) of the material by the dosage of the  $NH_4^+$  ion in the solution. The quantity of  $NH_4^+$  ions captured in the preferential sites by dosage is measured while using the distillation.

The X-Ray Diffraction revealed mixed clays with several clayey minerals (the kaolinite, the bentonite, the vermiculite and the illite-montmorillonite). The clay A2, for example, contains a most elevated rate of bentonite (18 %), followed of the clay A4 (17 %), and of the clay A3 (1,9 %).

The analysis of the clays samples by the, the X-Ray Fluorescence showed that the content in silicon is superior to 45 % in all of clays samples non activated (table 2). The content made of aluminum varies of 8 to 25 %. The content of the other elements (*Na, Mg, Fe, K, Ti, Ca, etc.*) in the samples indicates that the natural clays studied are of silicates of aluminum enriched (Zuka, 2016). The clay A2 contains more sodium than the other clays. According to the observations of Gaombale (2004), the cation  $Na^+$  has the easiness to exchange with another cation in an aqueous solution. This author explains that the link of pressed them in the clays depends of the electrostatic interactions. So the affinity of the link varies according to the lyotropic set following:



The lyotropic set is a classification of the ions by order of their capacity to set strongly on a molecule (Zhang & Cremer, 2006). In this set, the  $Al^{3+}$  ions have the most elevated link affinity and  $Na^+$  the weakest. We also observe that the non activated clay A3 contains more of iron (4,63 %) and less calcium (0,03 %) that the other clays.

Table 2. Elements contained in the different clays samples not activated

Elements	Content (%)					
	A1na	A2na	A3na	A4na	A5na	A6na
<i>Na</i>	0,05	0,12	0,03	0,03	0,03	0,07
<i>Mg</i>	0,91	7,82	0,86	0,51	0,43	3,63
<i>Al</i>	14,91	8,23	15,50	23,87	19,07	10,24
<i>Si</i>	50,40	50,93	46,74	45,54	47,70	57,08
<i>Cl</i>	0,01	0,00	0,02	0,02	0,03	0,01
<i>K</i>	4,08	3,74	1,11	1,26	0,67	2,22
<i>Fe</i>	3,50	2,06	4,63	1,00	0,50	0,72

In all infrared Spectrum of the clays (figure 1), we observed a vibration of big amplitude around  $1000\text{ cm}^{-1}$ . We also observed some vibrations: between  $675\text{ cm}^{-1}$  and  $784\text{ cm}^{-1}$ ; around  $909\text{ cm}^{-1}$ ,  $1634\text{ cm}^{-1}$ ,  $3386\text{ cm}^{-1}$ , and  $3678\text{ cm}^{-1}$ . We assign the vibrations: around  $1000\text{ cm}^{-1}$  to the vibrations of the valence strips  $Si - O - Al$ ; between  $675\text{ cm}^{-1}$  and  $784\text{ cm}^{-1}$  to the vibrations of the distortion strips  $Si - O - Al$  and  $Si - O - Si$ ; at  $909\text{ cm}^{-1}$  to the vibrations of the distortion strips  $Al - OH$ , at  $3678\text{ cm}^{-1}$  to the vibrations of the valence strips  $Al - OH$ ; at  $1634\text{ cm}^{-1}$  and around  $3386\text{ cm}^{-1}$  are a characteristic of the vibrations  $O - H$  that represents the sites of absorption and retention of water in the clays. The difference of amplitude of the stripes observed to  $1634\text{ cm}^{-1}$ , and to  $3386\text{ cm}^{-1}$  is due to the presence or the absence of the  $K^+$  ions to the surface of the clays. The clays A1 and A2 are rich in potassium, therefore they have a weak capacity to keep water in the space interfoliaire. On the other hand the clay A5 contains less  $K^+$  ions and therefore a very big capacity of absorption and the retention of water (Morel, 1996 ; Rinnert 2004). The stripes to  $1634\text{ cm}^{-1}$  and to  $3386\text{ cm}^{-1}$  increase in intensity with the activation of the clays. What could mean that the sites of absorption and retention of water increase following the activation of the clays that puts the ions outside and of other impurities (Elfil et al., 1995).

The MTE pictures of the clays showed heterogeneities in the materials, to the interfaces between the grains. These heterogeneities are supposed to have an important role in the interconnection of the pores in the materials. The size of the pores is one of the factors that determines the dynamics of the exchangeable ions. The activation of the clays has for morphological effect to increase the volume of the pores of the clays and therefore the increase of the specific area of the clays.

The chemical technique of dosage by the  $NH_4^+$  ions permitted to determine the cation exchange capacity (CEC) of the activated clays and not activated clays. The gotten results are presented in the table 3.

Table 3. Cation exchange capacity (CEC) of the activated clays and not activated clays

Clays	CEC (még/100 g)	
	Not activated clays	Activated clays
A1	7,00	20,40

A2	17,20	38,00
A3	28,00	21,80
A4	9,80	23,20
A5	5,20	12,40
A6	6,20	16,40

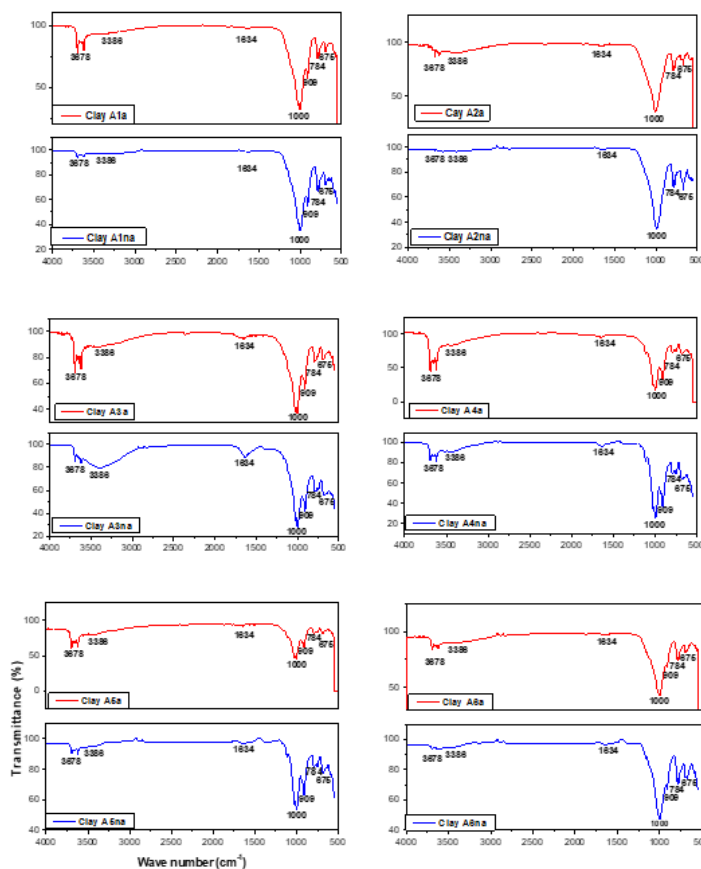


Figure 1. Infrared Spectrum of the clays

These results show that the values of the cation exchange capacity of the activated clays are superior to those of the not activated clays. It confirms the effect of the activation on the clays that, on the one hand, decrease the percentage of potassium in the clays while increasing the capacity of absorption and the retention of water, and on the other hand, improve the cation exchange capacity by the increase of the specific area of the clays (Elfil et al., 1995). The activated clay A2 present a cation exchange capacity superior to those of the other activated clays. It would be due to the strong content in bentonite in relation to the other activated clays.

We also observe that the activated clay A3 present a cation exchange capacity lower to the one of the not activated clay A3 contrary to what is observed for the other clays. The big cation exchange capacity of the not activated clay A3 would be due to the strong content made of iron.

These authors showed indeed that the incorporation of iron in the structure of some clays of the tropical soils rich in iron influences their crystallization and confer them a elevated big cation exchange capacity.

The reduction of the cation exchange capacity of the clay A3 during the process of activation is probably due to the phenomenon of ferrolyse (change bound to the production of protons generated at the time of the cycles of reduction and oxidation of iron) (Brinkmann, 1970; Espiau & Pedio, 2010). According to these authors, to every cycle of reduction and oxidation of iron, some pressed exchangeable ( $Na^+$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ , etc.) of the constituent clayey would be expelled of their sites to be replaced by the ions, reducing thus the cation exchange capacity.

Thus, the clay A3 rich in iron would already have undergone the phenomenon of ferrolyse in its natural environment following seasonal alternations of reduction and oxidation of iron. It had to undergo the phenomenon of ferrolyse again during its chemical activation in the hydrochloric acid, what appears by the reduction its cation exchange capacity.

## 2.2. Adsorption experiments and results

Adsorption experiments consisted in pulverizing a quantity of the clay in an aqueous solution of nickel sulphate or in an solution of hydrometallurgical effluents, and to get a homogeneous suspension. This suspension has been filtered then to get a filtrate to analyze by the atomic absorption spectroscopy to deduct the concentration of the  $Ni^{2+}$  ions adsorbed of it on particles of clays. For every clay sample, a quantity (of 0,1 g; 0,2 g; 0,3 g; 0,4 g; 0,5 g; 0,6 g; 0,7 g; 0,8 g ; 0,9 g ; 1g) has been pulverized either in 10 mL an aqueous solution of nickel sulphate initially to  $15\text{ mgL}^{-1}$  in  $Ni^{2+}$  ions, either in a hydrometallurgical solution always initially to  $15\text{ mgL}^{-1}$  in  $Ni^{2+}$  ions. The concentration of the  $Ni^{2+}$  ions in the filtrate has been measured then by the atomic absorption spectroscopy. The concentration of the  $Ni^{2+}$  ions adsorbed on the clay has been gotten while making the difference between the concentration of the  $Ni^{2+}$  ions in the filtrate, measured by the atomic absorption spectroscopy, and the initial concentration of the  $Ni^{2+}$  ions, of  $15\text{ mgL}^{-1}$ . The values of this concentration are presented in the tables 4, 5, 6 and 7 according to the quantity of clay pulverized in the considered solution.

**Table 4.** Concentration  $C(\text{mgL}^{-1})$  of the  $Ni^{2+}$  ions adsorbed according to the quantity of the activated clay that has been pulverized in the aqueous solution of nickel sulphate initially to  $15\text{ mgL}^{-1}$  in  $Ni^{2+}$  ions.

Mass (g)	A1a	A2a	A3a	A4a	A5a	A6a
0,1	11,16	6,61	8,7	12,51	8,63	10,04
0,2	11,28	8,98	9,7	13,16	9,84	11,69
0,3	11,84	10,7	9,7	13,79	10,57	12,4
0,4	11,95	10,99	10,52	14,01	11,13	12,97
0,5	12,37	11,61	10,64	14,35	11,58	13,5
0,6	12,63	12,14	10,75	14,44	11,95	13,66
0,7	12,64	12,44	10,99	14,49	12,39	13,85
0,8	12,66	12,45	11,03	14,54	12,57	14,00
0,9	12,67	12,46	11,05	14,59	12,61	14,11
1	12,7	12,48	11,06	14,62	12,69	14,14

**Table 5.** Concentration  $C(\text{mgL}^{-1})$  of the  $Ni^{2+}$  ions adsorbed according to the quantity of the not activated clay that has been pulverized in the aqueous solution of nickel sulphate initially to  $15\text{ mgL}^{-1}$  in  $Ni^{2+}$  ions.

Mass (g)	A1na	A2na	A3na	A4na	A5na	A6na
0,1	9,13	1,08	11,16	3,75	6,44	9,75
0,2	9,88	1,15	13,63	3,88	7,13	10,22
0,3	10,37	1,21	14,08	4,09	9,51	10,62
0,4	10,83	1,26	14,56	4,24	9,59	11,31
0,5	10,99	1,29	14,63	4,39	10,09	12,18
0,6	11,21	1,31	14,7	4,49	10,34	12,49
0,7	11,35	1,37	14,67	4,59	10,75	13,02
0,8	11,44	1,69	14,69	5,61	10,76	13,28
0,9	11,57	2,03	14,69	5,98	10,77	13,34
1	11,69	2,04	14,69	5,73	10,79	13,36

**Table 6.** Concentration  $C(\text{mgL}^{-1})$  of the  $Ni^{2+}$  ions adsorbed according to the quantity of the activated clay that has been pulverized in the hydrometallurgical solution initially to  $15\text{ mgL}^{-1}$  in  $Ni^{2+}$  ions.

Mass (g)	A1a	A2a	A3a	A4a	A5a	A6a
0,1	3,56	5,19	1,02	4,18	2,26	1,26
0,2	4,89	5,97	1,47	5,34	2,87	1,76
0,3	5,35	6,29	1,93	5,69	3,06	2,42
0,4	5,67	6,43	2,95	5,97	3,32	2,85
0,5	5,91	6,49	3,49	6,17	3,75	3,37
0,6	6,09	6,55	3,71	6,37	4,18	3,68
0,7	6,18	6,61	4,04	6,43	4,35	3,97
0,8	6,25	6,62	4,41	6,45	4,62	4,47
0,9	6,27	6,64	4,74	6,48	4,75	4,55
1	6,28	6,65	5,16	6,49	4,79	4,73

**Table 7.** Concentration  $C(\text{mgL}^{-1})$  of the  $\text{Ni}^{2+}$  ions adsorbed according to the quantity of the not activated clay that has been pulverized in the hydrometallurgical solution initially to  $15 \text{ mgL}^{-1}$  in  $\text{Ni}^{2+}$  ions.

Masse (g)	A1na	A2na	A3na	A4na	A5na	A6na
0,1	3,46	2,88	2,19	3,15	1,78	1,35
0,2	4,85	3,56	3,09	3,86	2,32	1,82
0,3	5,33	4,53+	3,58	4,55	2,98	2,77
0,4	5,58	4,95	4,16	4,95	3,21	3,16
0,5	5,99	5,26	4,77	5,16	3,64	3,44
0,6	6,01	5,44	5,33	5,49	3,83	3,58
0,7	6,13	5,61	5,69	5,68	3,94	3,72
0,8	6,16	5,75	6,22	5,77	4,11	3,87
0,9	6,19	5,88	6,52	5,94	4,29	3,95
1	6,21	5,97	6,58	6,05	4,37	3,98

### 3. Results and Discussion

In the tables 4, 5, 6 and 7, the values of the concentration of the  $\text{Ni}^{2+}$  ions adsorbed increase and stretch toward a certain saturation when the quantity of clay pulverized in the aqueous solution increases.

These tables show also that the clays adsorbed a lot more the  $\text{Ni}^{2+}$  ions in the aqueous solution of nickel sulphate than in the hydrometallurgical solution and that the activated clays, adsorbed the  $\text{Ni}^{2+}$  ions more than the not activated clays with the exception of the clay A3 that behaves differently.

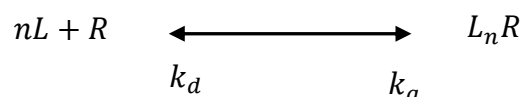
We suppose that the hydrometallurgical solution contains the  $\text{Ni}^{2+}$  ions and other  $\text{Z}^{2+}$  metallic ions. What makes that the adsorption of the  $\text{Ni}^{2+}$  ions on the clays is weak when they are pulverized in an hydrometallurgical solution that when they are pulverized in an aqueous solution of nickel sulphate. There was competition therefore between the ions  $\text{Ni}^{2+}$  and  $\text{Z}^{2+}$  contained in this solution.

The behavior of the concentration of the  $\text{Ni}^{2+}$  ions on the clays can be described while using a variant of the logistical model of growth of Pierre François Verhelst given by the equation :

$$y = a_1 + \frac{a_2 - a_1}{1 + \left(\frac{c}{m_0}\right)^n} \quad (1)$$

The conception of this logistical model of growth rests on the equation of Hill-Langmuir that herself drifts of the law of action of mass. Indeed, the model of Hill-Langmuir puts in evidence an equation of balance of the adsorption and the desorption of a species (L) named « Ligand » by another species (R) named « Receptor ». The « Ligand » species can be in variable concentration, while the species « Receptor » whose quantity is constant and is extensively worn out by the quantity of the « Ligand » species (Rudolf et al., 2012 ; Muntumosi

et al. 2021). The sites « Receptor » are in the clay, while the « Ligand » species are  $\text{Ni}^{2+}$  ions.



The factor  $n$  named coefficient of Hill, represent the number of coordinations for the « Ligand » species in a Receiving site « Receptor ». It provides a means to quantify the degree of interaction. The parameters  $k_a$  and  $k_d$  are respectively, the rate of adsorption and the rate of desorption.

The law of mass action is expressed as follows :

$$[L_nR] = [R_0] \frac{[L]^n}{[L]^n + K_d} = [R_0] \frac{[L]^n}{[L]^n + (K_a)^n} \quad (2)$$

Where  $[L_nR]$  Represent the concentration of the complex « Ligand-Receptor » ;  $[R_0]$  the total concentration of sites « Receptor » ;  $[L]$  the concentration of the « Ligand » ;  $K_d$  the constant of balance of dissociation of the complex « Ligand-Receptor » and  $K_a$  the constant of balance of association of the « Ligand » and the « Receptor » to form the complex « Ligand-Receptor ».

In terms of concentrations, the constants  $K_d$  and  $K_a$  are given by :

$$K_d = \frac{[L]^n[R]}{[L_nR]} \text{ et } K_a = \frac{[L_nR]}{[L]^n[R]} \quad (3)$$

The equation of Hill-Langmuir is used to determine the number of coordinations  $n$  of the Ligand binding to the macromolecule considered like receptor.

The modifications of the law of mass action [Eq. (2)] permit the application of the model of Hill-Langmuir in the description of the saturation sigmoïde phenomena and hyperbolic in experimental conditions (Morgan et al., 1975).

These modifications succeed to « the equation of Morgan-Mercer-Flodin » that expresses itself of the following manner :

$$[L_nR] = [R_0] \frac{[L]^n}{[L]^n + K_d} + \beta K_d \frac{1}{[L]^n + K_d} \quad (4)$$

We can demonstrate easily that the equation of Morgan-Mercer-Flodin can take the following shape :

$$[L_nR] = [R_0] + \frac{\beta - [R_0]}{1 + \frac{[L]}{K_d}} \quad (5)$$

Where  $\beta$  is a parameter of transfer on the axis of the ordinates.

While comparing the equation of the logistical model of growth [Eq. (1)] to the equation of Morgan-Mercer-Flodin [Eq. (5)], we can say that :

$$\left(\frac{c}{m_0}\right)^n = \frac{[L]^n}{K_d} ; a_1 = [R_0] \text{ et } a_2 = \beta \quad (6)$$

The Morgan-Mercer-Flodin equation writes itself then :

$$[L_n R] = [R_0] + \frac{\beta - [R_0]}{1 + \left(\frac{c}{m_0}\right)^n} \quad (7)$$

Where  $m_0$  represents the necessary quantity of clay to pulverize in an aqueous solution so that the concentration of the  $Ni^{2+}$  ions adsorbed on the clay is close to the half of the initial concentration of the  $Ni^{2+}$  ions in the aqueous solution and  $C$ , the concentration of the ions in the filtrate.

In this equation of Morgan-Mercer-Flodin [Eq. (7)], we observe that the concentration of the complex  $[L_n R]$  formed stretches toward a very weak value limits  $y_1 = [R_0]$  when the concentration of the  $Ni^{2+}$  ions in the filtrate is sufficiently big ( $C \rightarrow \infty$ ).

Without  $Ni^{2+}$  ions in the filtrate ( $C = 0$ ), the complex formed in receiving sites stretches toward a saturation value limits  $y_2 = \beta$ .

We then have  $y_2 - y_1 = \beta - [R_0]$  is the concentration of the reactional sites.

To analyze the experimental data, we used the software analysis of data (OriginPro8). We note that the logistical function of growth proposed  $y$  fits better to the values measured for the concentration of the  $Ni^{2+}$  ions in the aqueous solution. A set of the figures has been gotten. In these figures, the values  $y$  stand for the concentration of the  $Ni^{2+}$  ions adsorbs according to the quantity of clay that has been pulverized in the aqueous solution.

Indeed, the concentration of the  $Ni^{2+}$  ions adsorbs is function of the total concentration of « Receiving » sites contained in the clay.

Thus, the figures 2 and 3 shows the behavior of the concentration of the  $Ni^{2+}$  ions adsorbs according to the quantity of clays that has been pulverized in the aqueous solution of nickel sulphate and in the hydrometallurgical aqueous solution. On these figures, the points indicate the measured values, while the strong curve that ensues of the logistical model of growth shows the behavior of the adsorption phenomenon of  $Ni^{2+}$  ions in the aqueous solution.

We observe on these figures that the concentration of the  $Ni^{2+}$  ions adsorbs increases a certain manner when the quantity of clay pulverized increases.

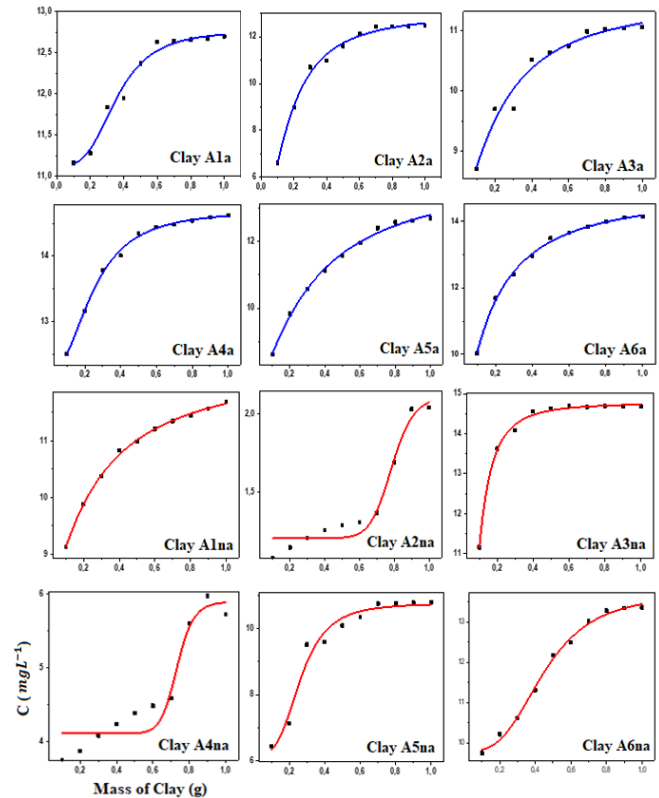


Figure 2. Behavior of the concentration of the  $Ni^{2+}$  ions adsorbs according to the quantity of clay activated and non activated that has been pulverized initially in the aqueous solution of nickel sulphate to  $15 \text{ mgL}^{-1}$  in  $Ni^{2+}$  ions

The tables below present the values gotten of the parameters intervening in the law of action of mass when we adjust the logistical function of growth to the experimental data for every sample of clay pulverized in the aqueous solution. Let's recall more that  $a_1 = [R_0]$  account for the total concentration of « Receiving » sites contained in the clay ;  $a_2 = \beta$  account for a saturation value limits of the complex formed in receiving sites and  $a_2 - a_1 = \beta - [R_0]$  the concentration of the reactional sites in the sample of clay.



**Table 8.** Parameters of the logistical function of growth adjusted to the experimental data of the activated clays in the aqueous solution of nickel sulphate initially to  $15 \text{ mgL}^{-1}$  in  $\text{Ni}^{2+}$  ions

Clays	$a_1$ ( $\text{mgL}^{-1}$ )	$\Delta a_1$ ( $\text{mgL}^{-1}$ )	$a_2$ ( $\text{mgL}^{-1}$ )	$\Delta a_2$ ( $\text{mgL}^{-1}$ )	$m_0$ (g)	$\Delta m_0$	n	$\Delta n$	$R^2$	$(a_2 - a_1)$ ( $\text{mgL}^{-1}$ )
A1a	11,12	0,11	12,77	0,99	0,26	0,02	3,34	0,80	0,98	1,65
A2a	4,27	1,75	13,01	0,38	0,18	0,04	1,72	0,47	0,99	8,74
A3a	7,86	1,61	11,55	0,76	0,23	0,11	1,39	1,09	0,95	3,69
A4a	12,23	0,12	14,71	0,05	0,24	0,01	2,29	0,28	0,99	2,48
A5a	7,39	0,76	14,09	0,76	0,26	0,03	1,25	0,35	0,99	6,7
A6a	7,29	1,63	14,95	0,38	0,16	0,04	1,21	0,31	0,99	7,66

**Table 9.** Parameters of the logistical function of growth adjusted to the experimental data of the not activated clays in the aqueous solution of nickel sulphate initially to  $15 \text{ mgL}^{-1}$  in  $\text{Ni}^{2+}$  ions

Clays	$a_1$ ( $\text{mgL}^{-1}$ )	$\Delta a_1$ ( $\text{mgL}^{-1}$ )	$a_2$ ( $\text{mgL}^{-1}$ )	$\Delta a_2$ ( $\text{mgL}^{-1}$ )	$m_0$ (g)	$\Delta m_0$	n	$\Delta n$	$R^2$	$(a_2 - a_1)$ ( $\text{mgL}^{-1}$ )
A1na	8,10	0,46	12,39	0,31	0,35	0,02	1,18	0,25	0,99	4,29
A2na	1,20	0,03	2,11	0,12	0,78	0,30	1,25	4,72	0,96	0,91
A3na	4,95	0,07	14,77	0,08	0,07	0,06	2,08	0,64	0,99	9,82
A4na	4,11	0,11	5,90	0,24	0,73	0,03	1,04	0,07	0,92	1,79
A5na	6,18	0,43	10,76	0,21	0,32	0,02	3,47	0,99	0,97	4,58
A6na	9,81	0,11	13,73	0,19	0,45	0,12	3,19	0,43	0,99	3,92

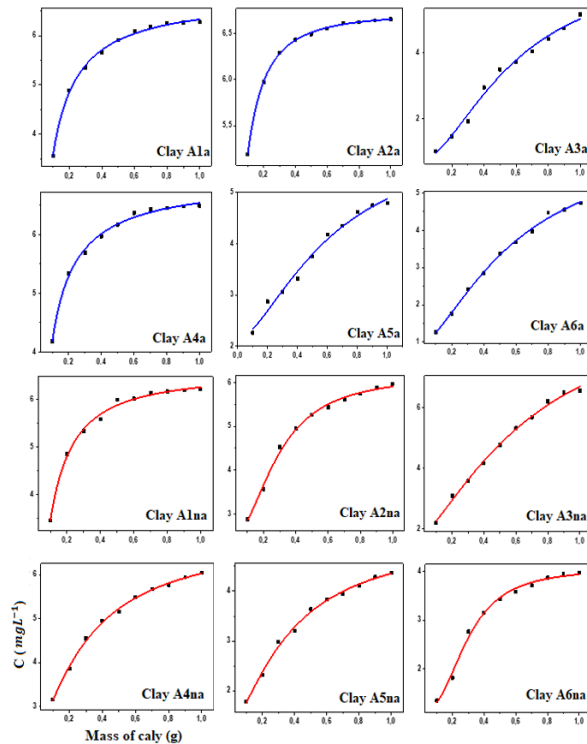
**Table 10.** Parameters of the logistical function of growth adjusted to the experimental data of the activated clays in the hydrometallurgical aqueous solution initially to  $15 \text{ mgL}^{-1}$  in  $\text{Ni}^{2+}$  ions

Clays	$a_1$ ( $\text{mgL}^{-1}$ )	$\Delta a_1$ ( $\text{mgL}^{-1}$ )	$a_2$ ( $\text{mgL}^{-1}$ )	$\Delta a_2$ ( $\text{mgL}^{-1}$ )	$m_0$ (g)	$\Delta m_0$	n	$\Delta n$	$R^2$	$(a_2 - a_1)$ ( $\text{mgL}^{-1}$ )
A1a	3,10	0,50	6,80	0,20	0,04	0,01	0,88	0,38	0,99	3,7
A2a	3,20	0,08	6,73	0,02	0,08	0,02	1,51	0,10	0,99	3,53
A3a	0,70	0,30	6,72	1,50	0,98	0,15	1,73	0,57	0,99	6,02
A4a	3,46	0,12	6,97	0,41	0,03	0,01	0,92	0,58	0,99	3,51
A5a	2,11	0,21	6,19	1,37	0,37	0,2	1,57	0,03	0,98	4,08
A6a	0,91	0,21	6,48	0,88	0,29	0,10	1,53	0,31	0,99	5,57

**Table 11.** Parameters of the logistical function of growth adjusted to the experimental data of the not activated clays in the hydrometallurgical aqueous solution initially to  $15 \text{ mgL}^{-1}$  in  $\text{Ni}^{2+}$  ions

Clays	$a_1$ ( $\text{mgL}^{-1}$ )	$\Delta a_1$ ( $\text{mgL}^{-1}$ )	$a_2$ ( $\text{mgL}^{-1}$ )	$\Delta a_2$ ( $\text{mgL}^{-1}$ )	$m_0$ (g)	$\Delta m_0$	n	$\Delta n$	$R^2$	$(a_2 - a_1)$ ( $\text{mgL}^{-1}$ )
A1na	0,95	0,64	6,56	0,28	0,07	0,02	1,19	0,54	0,99	5,61
A2na	2,46	0,23	6,17	0,16	0,28	0,01	2,04	0,33	0,99	3,71
A3na	1,72	0,39	10,01	2,39	0,73	0,28	1,35	0,38	0,99	8,29
A4na	2,33	0,36	6,88	0,36	0,32	0,02	1,31	0,26	0,99	4,55
A5na	1,25	0,32	5,10	0,43	0,60	0,03	1,43	0,36	0,99	3,85
A6na	1,14	0,15	4,05	0,10	0,59	0,01	2,57	0,41	0,99	2,91

The tables 8, 9, 10 and 11 shows that the clays samples A2a, A6a and A3na have the very elevated concentrations of reactional sites  $a_2 - a_1$ . What means that the A2a clays, A6a and A3na absorb a lot more  $\text{Ni}^{2+}$  ions contained in the aqueous solution of nickel sulphate as in the hydrometallurgical aqueous solution that the other clays samples. The concentrations of the reactional sites are located around  $8,74 \text{ mgL}^{-1}$  for the clay A2a,  $9,82 \text{ mgL}^{-1}$  for the clay A3na and  $7,66 \text{ mgL}^{-1}$  for the clay A6a in the aqueous solution of nickel sulphate. While the concentrations of the reactional sites are located around  $8,29 \text{ mgL}^{-1}$  for the clay A3na,  $6,02 \text{ mgL}^{-1}$  for the clay A3a,  $5,61 \text{ mgL}^{-1}$  for the clay A1na and  $5,54 \text{ mgL}^{-1}$  for the clay A6a in the hydrometallurgical aqueous solution. The concentration raised of the reactional sites for the clays A2a and A3na explains itself by the fact that these clays have a big cation exchange capacity. It confirms the results of the chemical technical of dosage by the  $\text{NH}_4^+$  ions (table 3).



**Figure 3.** Behavior of the concentration of the  $Ni^{2+}$  ions adsorbs according to the quantity of clay activated and non activated that has been pulverized initially in the hydrometallurgical aqueous solution to  $15\text{ mgL}^{-1}$  in  $Ni^{2+}$  ions

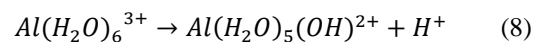
While the clays A6a and A1na that present the weak cation exchange capacity, on the other hand present high  $Na^+$  ion contents just after A2a (table 2).

We observe in these tables that the activated clays present weak quantities  $m_0$  in relation to the non activated clays in the two aqueous solutions with the exception of the clay A3. Very small quantities of the activated clays are sufficient therefore for adsorb a great deal of  $Ni^{2+}$  ions in the aqueous solution. While the adsorption of  $Ni^{2+}$  ions by the non activated clays is very weak and is governed by the complex phenomena of exchange between the non activated clays and the aqueous solution. Very big quantities of the non activated clays are not sufficient for adsorb a great deal of  $Ni^{2+}$  ions in the aqueous solution.

Indeed, We observed like other authors that the adsorption of the  $Ni^{2+}$  ions is optimal on the clays that present either a big cation exchange capacity either a strong content in  $Na^+$ ,  $Al^{3+}$  and  $Fe^{2+}$  ions, and either again a weak content in  $K^+$  ions. This adsorption capacity of can explain itself by the

easiness of the  $Na^+$  ions to exchange itself with other ions in an aqueous solution according to the set lyotropique (Gaombale, 2004 ; Zhang & Cremer, 2006). The  $K^+$  ions as for them, prevent the penetration of water in the interfoliaire space and the inflation of the clays (Rinnert 2004). The clays having a strong content in  $Fe^{2+}$  ions present a big cation exchange capacity.

These authors showed that the incorporation of iron in the structure of some clays of the tropical soils rich in iron influences their crystallization and confer them a high cation exchange capacity. The octahedrals layers that form the leaflets of the clayey minerals are formed of the octahedrons constituted of an  $Al^{3+}$  ion in the center surrounded with six groups hydroxyles ( $-OH$ ) in the summits. The trivalent aluminum can stand to the neighborhood of the complex adsorbant while neutralizing three negative loads. As every  $H^+$  ion is of six molecules of water placed to the summits of the octahedron, we can admit that aluminum is fixed through the intermediary of bridge of hydrogen that binds the oxygens of the clayey minerals and water. The  $Al^{3+}$  ion removed of six molecules of water behaves like a weak acid :



The clays A1 and A2 non activated are rich in potassium (table 2), therefore they have a weak capacity to keep water in the interfoliaire space. An optimal adsorption of the  $Ni^{2+}$  ions on the clays has also been observed for the activated clays that present the values of the cation exchange capacity superior to those of the non activated clays. The activation technical of the clays decreases the percentage of potassium in the clays and increase the capacity of absorption and the retention of water. It also improves the cation exchange capacity by the increase of the specific surface of the clays (Elfil at al., 1995). The activated clay A2 present a cation exchange capacity superior to those of the other activated clays.

Other results showed that the adsorption of  $Ni^{2+}$  is dominated mainly by the ionic exchange. The adsorption of surface only intervenes little. This adsorption of surface is due to the isomorphic substitution and to the rupture of the links of the functional groupings of surface,  $Al - OH$ ,  $O - H$  and

Si – O – Al of the clay. In this case, the  $Ni^{2+}$  ions are adsorbed by ionic exchange and by electrostatic attraction or strengths of Van der Waals.

#### 4. Conclusion

The objective of this work had to study the adsorption of the  $Ni^{2+}$  ions of hydrometallurgical effluents on natural clays harvested thru Kinshasa and towards Kongo-central in Democratic Republic of Congo. This study has been achieved in order to verify the performance of these natural clays in the elimination of metal cations of hydrometallurgical effluents and the effect of the chemical activation of the clays on the phenomenon of adsorption of the metallic ions in an aqueous solution. The model of Hill-Langmuir has been used in order to determine the favorable conditions to a maximal elimination of metal cations. Two parameters have been studied, the concentration of metal cations as well as the mass of clay that has been pulverized in the aqueous solution.

The results gotten in this research showed that the samples of natural clays harvested have a big efficiency in the elimination of metal cations. This efficiency increase with the augmentation in clay mass that has been pulverized in the aqueous solution. The concentration of the reactional sites of the clays found for the aqueous solution of nickel sulphate is of  $8,74 \text{ mgL}^{-1}$  for the clay A2a and of  $9,82 \text{ mgL}^{-1}$  for the clay A3na. In the hydrometallurgical aqueous solution it is of  $8,29 \text{ mgL}^{-1}$  for the clay A3na,  $6,02 \text{ mgL}^{-1}$  for the clay A3a.

The results gotten in this research also showed that the chemical activation of the natural clays only increase their capacity to adsorb the  $Ni^{2+}$  ions. The activated clays adsorb  $Ni^{2+}$  ions more than the non activated clays with the exception of the clay A3 that behaves differently. These activated clays presented weak quantities  $m_0$  in relation to the non activated clays in the two aqueous solutions. The A3 clay makes exception again for the quantities  $m_0$ .

The gotten results also revealed that on the clays, the  $Ni^{2+}$  ions are adsorbed by the ionic exchange phenomenon and by electrostatic attraction or strengths of Van der Waals.

The optimal results have been gotten for the activated clays and those presenting following features : a strong content in  $Na^+$ ,  $Fe^{2+}$  and  $Al^{3+}$  ions and a weak content in  $K^+$  ions.

This elimination technical of  $Ni^{2+}$  ions can be generalized to cover other metals, especially the heavy metals as the Cobalt, the Copper, the Mercury etc. A development of the process studied in this research permits to conceive filters made of clay for industrial technological applications. These applications can take place in the treatment of waste waters of the electrochemical industries and of the hydrometallurgical effluents of the mining activities.

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