

Characterization and Modification of Moroccan Clay by an Organic Molecule and Its Application to the Removal of Iron and Copper in Aqueous Medium

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ABSTRACT: The first objective presented in this study is first to improve the surface properties of pyrophyllite following the treatment carried out which developed the active sites on the surface of this material. The treated material was characterized by DRX, X-ray fluorescence, IRTF and SEM. The pyrophyllite was modified by coating with aminosilane 3- (2-aminoethylamino) propyl-methyldimethoxysilane (APMDS). It has been suggested that the formation of hydrogen bonds took place between the hydroxyl groups and/or oxygen atoms within the structure of pyrophyllite and the hydroxyl groups of the APMDS. The second objective of this study is the application of this material in the removal of iron (Fe(III)) and copper (Cu(II)) in aqueous solutions, and the highlighting of the effectiveness of the treated material compared to the natural clay vis-a-vis the adsorption of these metal ions. Various parameters are determined and optimized: the contact time, the pH, the density of the pulp and the initial concentration of the solute. These experiences have lead to the fact that the adsorption capacities of the Fe(III) and Cu(II) are much more important in the case of the pyrophyllite-APMDS in comparison with those of natural pyrophyllite . Thus, the rate of elimination of Fe (III) increases from 54% for natural pyrophyllite to 90% for pyrophyllite-APMDS. For Cu (II) the removal rate is 60% in the case of pyrophyllite-APMDS and 18% in the case of natural pyrophyllite. The studies carried out also showed that the two treated and untreated adsorbents have more affinity with iron than with copper.

KEYWORDS: Modified Clay, Pyrophyllite, Aminosilane, characterization, adsorption, heavy metals.

I. INTRODUCTION

Since the industrial revolution to this day, the fresh waters are all the time exposed to the pollution with its different forms. The waters which are most exposed to pollution due to heavy metals are the waters near to landfill sites if their leachate is not equipped with a modern wastewater treatment plant that uses processes suitable for heavy metal treatment and mining wastewater. Also adding the water streams that cross the fields where we use fertilizers, insecticides and pesticides containing heavy metals. Water is a vector transporting these heavy metals from their sources to our human bodies through the food chains (fruit, vegetables, algae, fish, meat, animal feed and drinking water). Even though heavy metals are traceable and do not constitute a real hazard in a specific environment, their toxicity develops through bioaccumulation in organisms until they reach critical concentrations that make them

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dangerous. To this end, their elimination of wastewater and drinking water becomes imperative and a major priority in order to ensure long-term protection of the ecosystem.

Heavy metals are also known as metallic trace elements (ETM). They are so named because they are found in low concentrations in the earth's crust. However, anthropogenic factors such as mining activity can lead to a considerable increase in metal concentrations in the waters and sediments of the affected area, in which case these elements can be considered as major elements in the environment studied.

In recent years, the production of copper and iron has increased drastically, thanks to its of mechanical, chemical, and electrical characteristics. As a result, quantities of these two metals have increased in the environment by polluting water, soil and air. Copper (Cu), in the field of electronics as well as fungicide (copper sulfate, especially used in the treatment of vines); Iron and its alloys, steels, stainless steels. The soluble compounds of copper and iron form the biggest threat for human health. To reduce the impact of this pollution, several methods have been used: Precipitation of heavy metals has long been the most widely used technique [1, 2]. Although this process is effective, it has disadvantages, in fact it produces large quantities of the sludge which has a very long settling time. The use of coal in the adsorption process is also highly demanded. Activated carbon has a high adsorption capacity due mainly to its large surface area, but this process remains very expensive. Attention was subsequently focused on the use of new adsorbents based on abundant natural materials. This is the case for natural or synthetic zeolites, volcanic ash and especially clays [3,4]. Nowadays, a new family of solid microporous with controlled porosity, similar to zeolites and commonly known as clays modified, is extensively studied by many researchers. Many studies on the adsorption relate information about the different methods of synthesis and characterization, as well, a wide variety of clays modified by cationic polymeric species has been implemented and used in several chemical reactions.

This work, which is in line with our previous work, focuses on the valorization of an abundant Moroccan clay belonging to the family phyllosilicates: pyrophyllite, this study consists of preparing another type of material: a complex organo-clay (Our choice focused on the change of pyrophyllite by coating with an organic molecule called the aminosilane (APMDS) 3-(2 - aminoethylamino) propyl-methyldimethoxysilane.) For the application to the removal of Iron and Copper from aqueous media by adsorption on the two adsorbents (pyrophyllite and modified pyrophyllite) (APMDS), and to determine the results of the influence of the time of the reaction, the pH of the solution, and the concentration of the metal on the adsorption of the latter on the two adsorbent.

II. MATERIALS AND METHODS

II-1. ORIGIN OF THE PYROPHYLLITE

The pyrophyllite used in this study was provided by the Office of Research and Participation in Mineral (BRPM). It is from the region of Gunfouda, south of Morocco. The choice of this aluminosilicate material has been dictated by the fact that:

- It is very abundant in Morocco and is inert with respect to the environment [5, 6].
- It has an adsorptive affinity towards heavy metals [7, 8, 9, 10-12] and organic molecules [13, 14].

II-2. EXPERIMENTAL PROTOCOL

This study is carried out at ambient temperature and in the presence of oxygen. The experiments are carried out in a series of small vials of 50 ml. The Copper and iron are added initially at concentrations ranging from $5 \cdot 10^{-5} \text{M}$ to 10^{-3}M , to which we add the same mass of adsorbent (10g/l). The pH of the suspension and then adjusted to the desired value by HNO_3 or NaOH . The solution obtained is analyzed by atomic absorption spectrometry after separation of the solid phase and the liquid phase by vacuum filtration.

Thus, a simple calculation will allow us to obtain the quantities of fixed product. The quantity of adsorbed product expressed in mg of solute per gram of adsorbent solid is given by the following equation:

$$Q_{\text{ad}} = (C_0 - M) \cdot V / m$$

Q_{ad} : Metal quantity by unit of mass of solid (in mg.g⁻¹).

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C_0 : Initial Concentration (mg. L⁻¹)

M : Residual Concentration in the equilibrium of metal (mg. L⁻¹)

V : Volume of the adsorbant (L)

m : Mass of the adsorbant (g)

The isotherm of adsorption of the considered product, is acquired by drawing the curve:

$$Q_{ad} = f(C_0) \text{ ou } Q_{ad} = f(C_e)$$

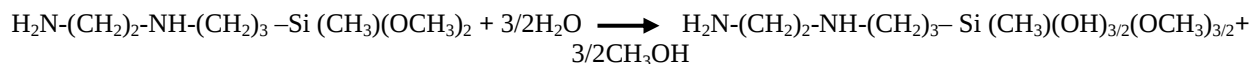
Or C_e : equilibrium concentration (mg.L⁻¹)

II-3 PREPARATION OF THE PYROPHYLLITE-APMDS

The preparation of the pyrophyllite-APMDS is performed following the processing of natural pyrophyllite by the organic molecule 3-(2-aminoethylamino) propyl-méthyldiméthoxysilane (APMDS).

a-Preparation of the solution of APMDS

Organic molecule hydrolysis (APMDS) We first prepared a solution of the organic molecule with a ratio of 1.5 mole of H₂O to one mole of APMDS, stirred at ambient temperature until obtaining a clear and homogeneous solution. The hydrolysis reaction is as follows :



The alcohol formed during the hydrolysis, between the hydroxide grouping of water and the methoxy grouping of the silane, has been eliminated in the rotavapor at a temperature of 40°C and a pressure of 220 mbar. We then added to the solution obtained the methanol to 50% by weight.

b-Synthesis of pyrophyllite-APMDS

After preparing the coating solution, we put it in contact with our material and we agitate the mixture at room temperature for 1 hour. We separate the solid phase by filtration and dry it for 90 min at 100 ° C. Thus we will have obtained our Pyrophyllite-APMDS.

CHARACTERIZATION OF PYROPHYLLITE AND PYROPHYLLITE- APMDS

Chemical analyzes of pyrophyllite and pyrophyllite-APMDS were performed using a Fluorescence spectrometer (Wavelength dispersion spectrometer - Axios type). (Table 1). Infrared spectroscopy (FTIR) analysis was performed in the 400-4000 cm⁻¹ range using a 'FTLA2000-102' spectrometer. The basic composition of our material has been determined by the analysis of dispersive energy (EDX) analysis was carried out using a diffractometer Philips PW-1130/00, working on the radiation of monochromatic Ka₁ of Copper (1,5406 Å). A counter (PM 8203) records a signal proportional to the intensity of the diffracted ray. The images of the surface of the material have been shown by scanning electron microscope analysis, the apparatus used is the JSM-6100 scanning microscope, the images represented during our work are obtained from samples previously covered with gold.

III. RESULTS AND DISCUSSIONS

III-1. QUANTITATIVE CHEMICAL ANALYSIS

Table 1 Chemical analysis (in% by mass) of pyrophyllite

Pyrophyllite	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	CaO	K ₂ O	MnO
	65,4	22,1	3,12	1,75	1,58	6,04	0,01

Table 1 Chemical analysis (in% by mass) of pyrophyllite

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According to these results we point out that: The weight ratio $\text{SiO}_2/\text{AlO}_3$ is of the order of 2.96, which shows that pyrophyllite is an aluminosilicate.

III-2. X-RAY DIFFRACTION ANALYSIS

X-ray diffraction analysis allows us to identify the different mineralogical phases contained in our materials.

FIG. 1 shows the X-ray diffraction spectra of natural pyrophyllite and pyrophyllite-APMDS.

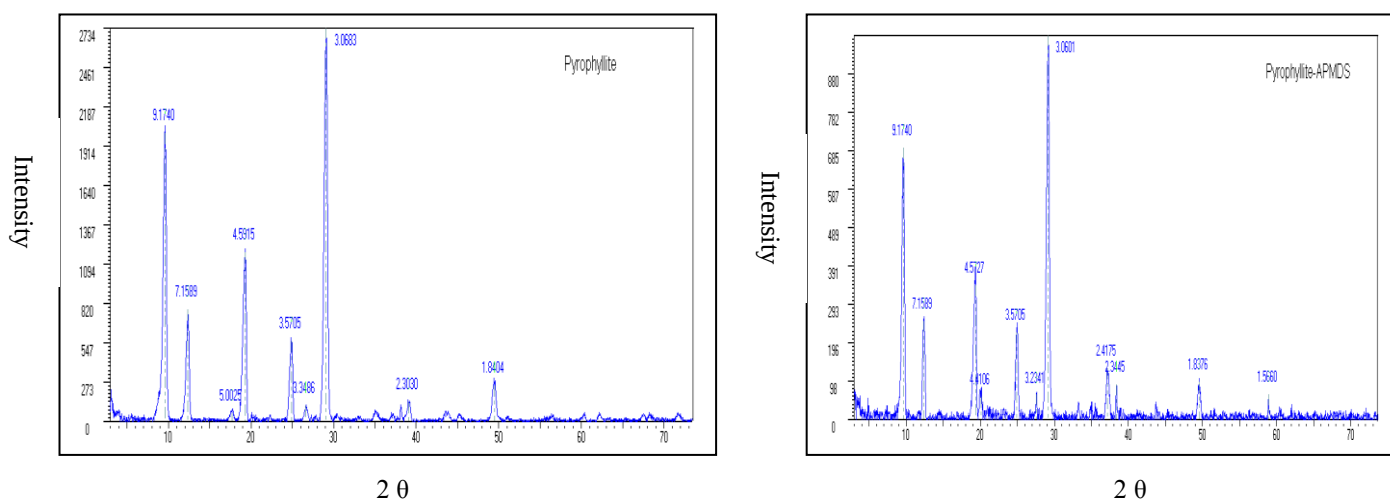


Fig.1 X-ray diffraction spectrum of pyrophyllite and pyrophyllite-APMDS.

According to the figure we notice that the positions of The peaks characteristics of pyrophyllite have not been changed, which proves that the structure of our clay has not been affected by this treatment.

However, there is a decrease in the intensity of the peaks characteristic of the pyrophyllite, which can be explained by the establishment of a slight disorder at the level of the mesh of the material, suggesting the establishment of chemical bonds between the organic molecule and the surface of the material [15]. These same results have been observed by the turks that have treated the pyrophyllite by a coupling agent : the aminosilane [16].

III-3. ANALYSIS BY INFRARED SPECTROSCOPY

The IR spectra (FIG. 2) were carried out using a Perkin-Elmer Fourier Transform 1720-X spectrometer over a range of 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1} . Samples were conditioned in the form of emulsion in a in a pellet of KBr (1/200 by weight).

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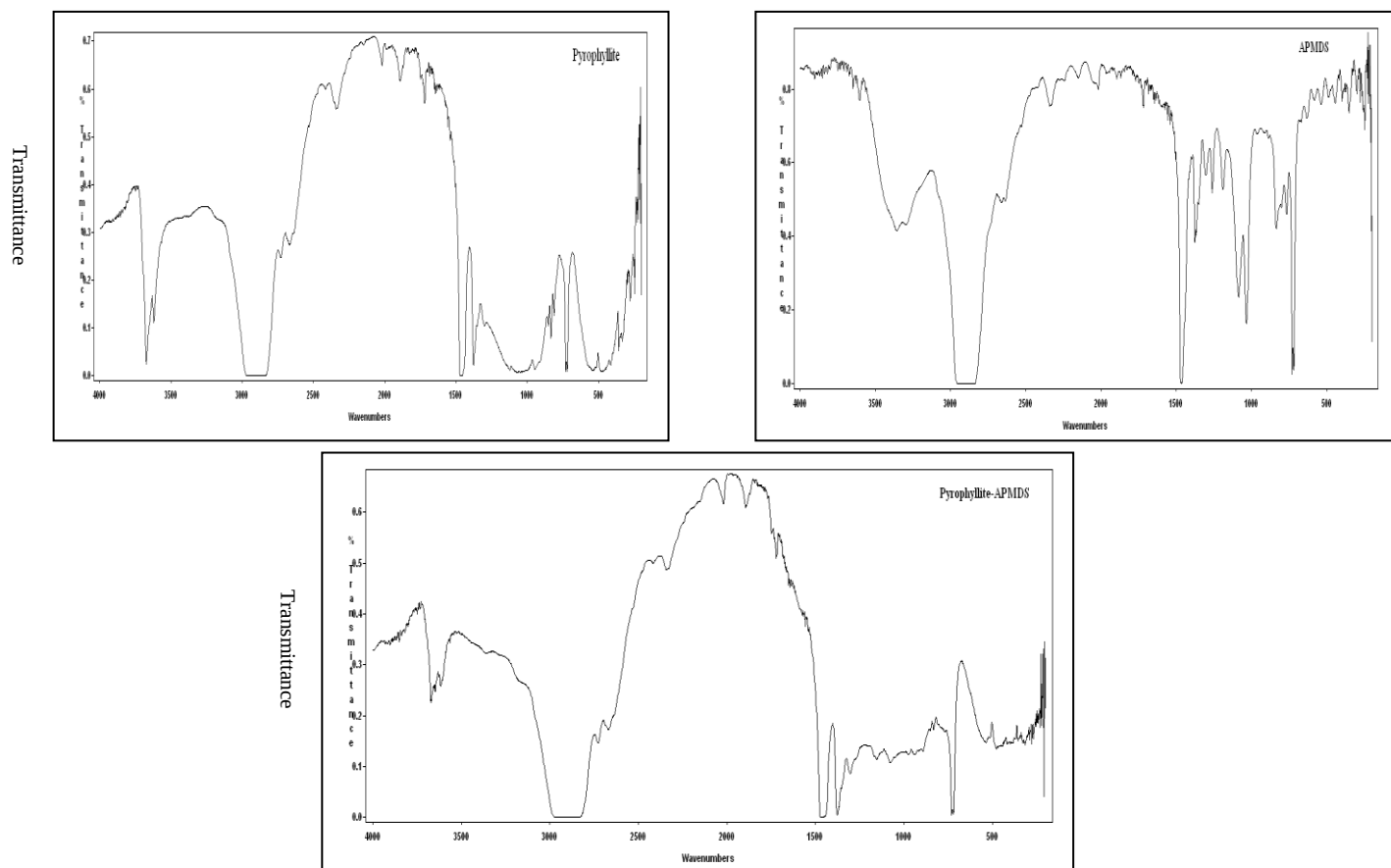


Fig.2 FTIR spectrum of pyrophyllite, APMDS and pyrophyllite-APMDS

The study of the IR spectra can inform us about the nature of the interaction between the organic molecule and our material [17]. In the light of these spectra we can note that :

- In the spectrum of pyrophyllite-APMDS, a broad band appears between 3130 and 3530 cm^{-1} and corresponds to the valence vibrations of the O-H bond.
- A band at 1610 cm^{-1} is attributed to vibrations C-NH-C.
- A small narrow band at 1670 cm^{-1} corresponding to O-H was also observed.
- The band located at 720 cm^{-1} in the three spectra corresponds to the plastic on which we deposit the sample before inserting it into the device. The same applies to the bands at 1490 and 2850 cm^{-1} which correspond to the paraffin oil used as much as emulsifier for the samples studied, as mentioned above.

All the peaks observed in the spectrum of pyrophyllite-APMDS are much smaller and much weaker than those of the APMDS, which suggests that hydrogen bonds are formed between the hydroxyl groupings and/or oxygen atoms of the pyrophyllite and the hydroxyl groupings of the APMDS. This leads to the formation of a monolayer on the surface of the clay [15].

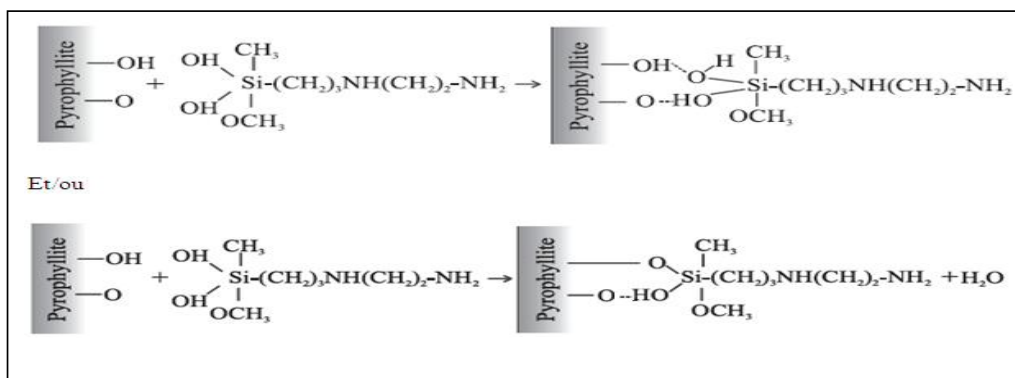
The binding reactions possible between the surface of the pyrophyllite and the molecule of the APMDS may be proposed as follows [18]:

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III-4. OBSERVATION BY THE SCANNING ELECTRON MICROSCOPE.

Figure 3 shows images of pyrophyllite, pyrophyllite-APMDS and the surface of the particles of each of these materials.

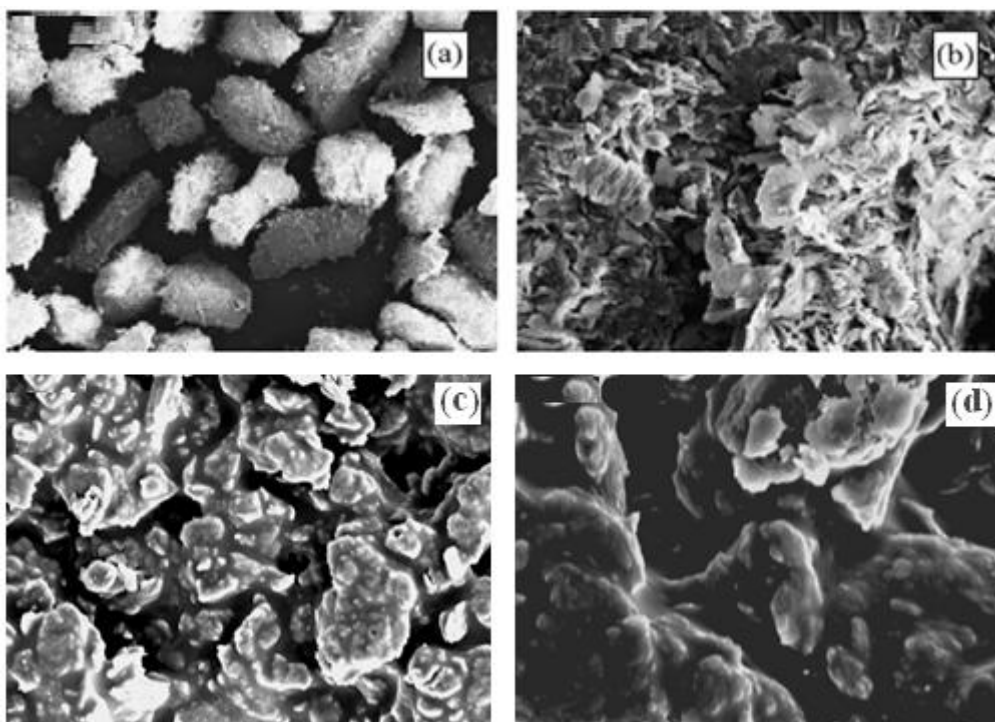


Fig.3 Scanning electron microscope imaging of pyrophyllite x400 (a), x1000 (b) and pyrophyllite-APMDS x400 (c) and x1000 (d).

It can be clearly observed that the pyrophyllite has acquired a surface that is more uniform and homogeneous, which confirms the recovery of its particles by a monolayer of APMDS.

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ADSORPTION OF IRON AND COPPER ON NATURAL PYROPHYLLITE AND PYROPHYLLITE-APMDS

In order to compare the relative affinities of some heavy metals with our materials, we studied the adsorption of Fe (III) and Cu (II) on each of our two natural and modified clays.

IV. STUDY OF THE ADSORPTION OF IRON

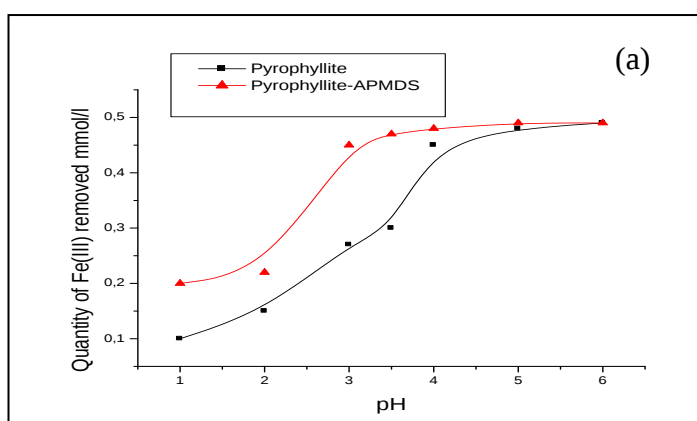
The adsorption of iron on the pyrophyllite and the pyrophyllite-APMDS has been achieved through the study of different parameters that affect its adsorption, in particular initial concentration, pH, agitation time and pulp density. The experimental conditions of this study are summarized in Table 2.

Parameters	Initial concentration in Fe (III)	Contact time	pH	Density of pulp
Initial Conc. in Fe(III), mol/l (5.10^{-5} - 10^{-3}) ^a	-	30	3	10
Contact time, minutes (10-120) ^a	5.10^{-4}	-	3	10
PH(2-6) ^a	5.10^{-4}	30	-	10
Density of pulp, g (3-40) ^a	5.10^{-4}	30	3	-

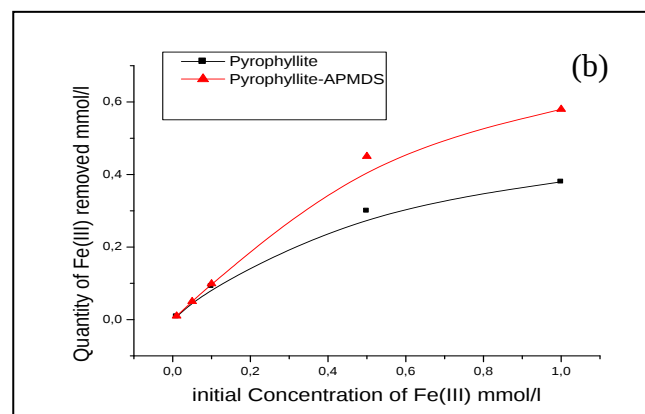
^a Varied parameter in this range.

Table 2 The experimental conditions applied during the experiments of adsorption of the Fe(III) on pyrophyllite and pyrophyllite-APMDS at a temperature of $21 \pm 1^\circ\text{C}$

The results of the study of adsorption of Fe(III) on the two materials are represented in the following graphs:



Density of pulp=10g/l, $[\text{Fe(III)}]_{\text{init}}=5.10^{-4}\text{mol/l}$,
Contact time= 30mn.



pH=3, Density of pulp=10g/l,
Contact time= 30mn.

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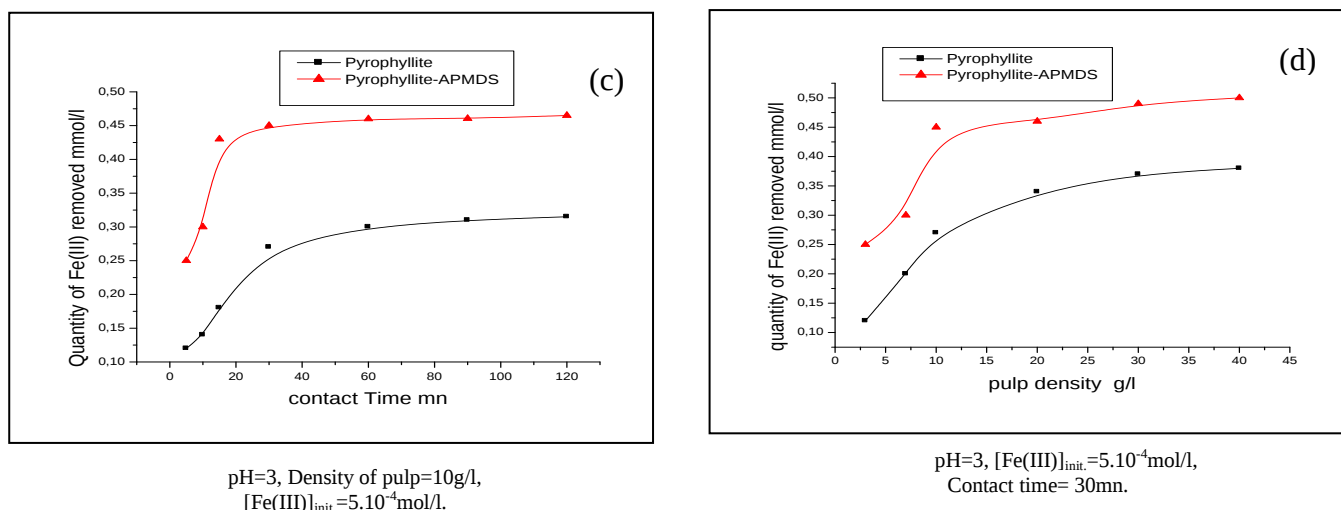


Fig.4 Effect of the various parameters: pH (a), initial metal concentration (b), contact time (c) and pulp density (d),

For an iron (III) initial concentration of 5.10^{-4} M and for $pH \leq 3.5$, the iron is present in solution in the free form Fe^{3+} . Beyond this pH and for this initial iron (III) concentration, the latter precipitates as ferric hydroxide $Fe(OH)_3$ [19]. At the end of these data and from the graph (a) relating to the study of the effect of pH, we can note that the maximum suppression of the ions $Fe(III)$ adsorption on our materials is observed at pH 3.5, knowing that its strong elimination beyond this pH is probably due to its precipitation in the form of hydroxide of iron $Fe(OH)_3$ [19]. Thus, the subsequent studies of adsorption of $Fe(III)$ iron at a concentration of 5.10^{-4} M, were carried out at pH 3 to facilitate the removal of iron by adsorption while avoiding its precipitation. The curves in the graph corresponding to the study of the adsorption of $Fe(III)$ as a function of the initial concentration of iron, it is apparent that the rate of elimination of these ions has been much more important in the case of the pyrophyllite-APMDS in comparison with natural pyrophyllite. Thus, for an iron concentration of 5.10^{-4} M, a rate of 90% removal of $Fe(III)$ has been observed in the case of the pyrophyllite-APMDS and 54% for natural pyrophyllite. In regard to the kinetic study, we were able to see that the equilibrium is reached at the end of the first 30 minutes for the pyrophyllite, then that for the pyrophyllite-APMDS balance is faster since it is reached after 15 minutes of contact. Moreover, we noted that the pulp density acts on the elimination of $Fe(III)$, since the percentage of adsorption increases by increasing the quantity of the adsorbent, which was explained previously by the availability of the sites which is completed by the establishment of a stage which corresponds to the adsorption of all the iron present in solution.

V. STUDY OF THE ADSORPTION OF COPPER

According to the adsorption studies of the other metals, the adsorption of the copper was carried out by studying the effect of the various parameters such as initial concentration, pH, stirring time and the density of pulp which act on its adsorption.

The experimental conditions of this study are summarized in Table 3.

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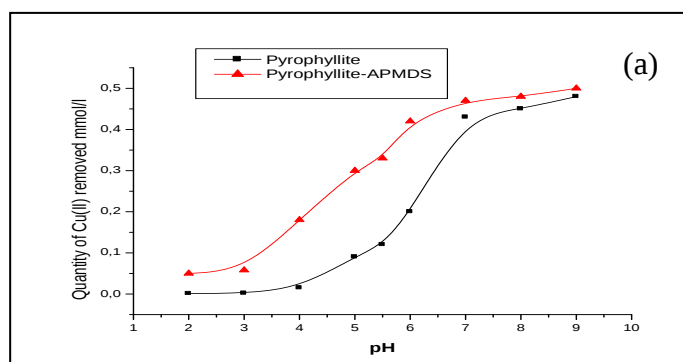
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Parameters	Initial concentration in Cu (II)	Contact time	pH	Density of pulp
Initial Conc. in Cu(II), mol/l (5.10^{-5} - 10^{-3}) ^a	-	60	5	10
Contact time, minutes (10-120) ^a	5.10^{-4}	-	5	10
PH(2-9) ^a	5.10^{-4}	60	-	10
Density of pulp, g (3-30) ^a	5.10^{-4}	60	5	-

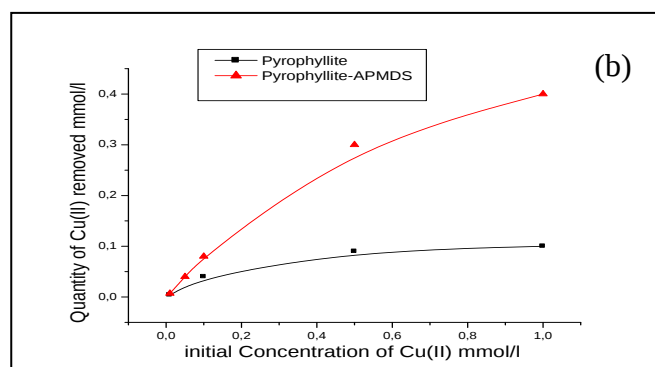
^a Varied parameter in this range.

Table 3 The experimental conditions realized in the experiments of adsorption of Cu(II) at a temperature of $21 \pm 1^\circ\text{C}$.

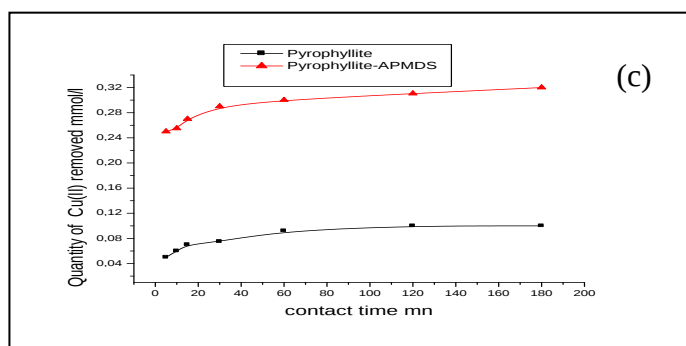
The results of the experiments carried out in this study are presented in the graphs of figure 5.



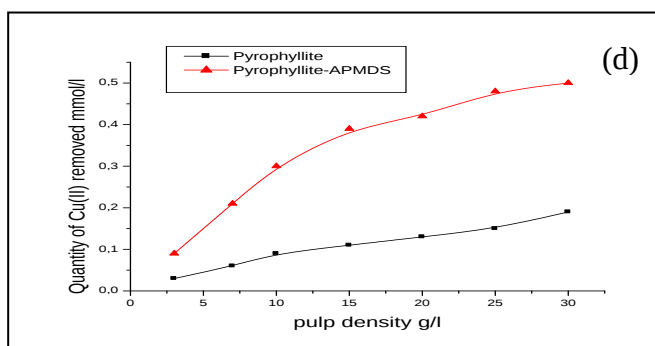
Density of pulp=10g/l, $[\text{Cu(II)}]_{\text{init.}}=5.10^{-4}\text{mol/l}$, Contact time= 60mn.



pH=5, Density of pulp=10g/l, Contact time= 60mn.



pH=5, $[\text{Cu(II)}]_{\text{init.}}=5.10^{-4}\text{mol/l}$, Density of pulp=10g/l.



pH=5, $[\text{Cu(II)}]_{\text{init.}}=5.10^{-4}\text{mol/l}$, Contact time= 60mn.

Fig.5 Effect of the various parameters: pH (a), initial metal concentration (b), contact time (c) and pulp density (d), on Cu (II) adsorption on pyrophyllite and pyrophyllite -APMDS at a temperature of $21 \pm 1^\circ\text{C}$.

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For an initial concentration of copper(II) of 5.10^{-4}M and for $\text{pH} \leq 5.5$, the predominant species in our solutions copper is the cation cupric Cu^{2+} . Beyond this pH, and for a same initial concentration of copper the latter undergoes a precipitation in the form of hydroxide, $\text{Cu}(\text{OH})_2$ [20]. From these data and with respect to the graph (a) study of the pH, we can note that the maximum removal of Cu(II) ions by adsorption on materials is observed at pH 5.5, knowing that its strong elimination beyond this pH is probably due to its precipitation as the hydroxide $\text{Cu}(\text{OH})_2$. Thus, in the sequel of this work, the study in aqueous solutions of the elimination of the Cu(II) at a concentration of 5.10^{-4}M , was carried out at pH 5 to facilitate its removal by adsorption while avoiding its precipitation. In addition, at the end of the kinetic study, we find that it is relatively slow in comparison with those of the iron as the balance is reached only after 60 min of contact.

We have also observed that the pulp density acts on the elimination of Cu(II), since the percentage of adsorption increases by increasing the quantity of the adsorbent, which was explained, as indicated above, by the availability of the active sites at the addition of the material, which phenomenon ends with the establishment of a plateau which corresponds to the adsorption of all the copper present in solution. We may note, from the data relating to the study of the effect of the initial concentration, as a concentration of copper of 5.10^{-4}M , the rate 60% of removal of Cu(II) in the case of the pyrophyllite-APMDS and a rate of 18% for the pyrophyllite natural. Thus, the rate of removal of ions of Cu(II) was much more important in the case of the pyrophyllite-APMDS in comparison with the natural material. Nevertheless, in comparison with the metal of the iron, our materials have a low affinity vis-a-vis the copper since it has been found, for a same pH value of 3 and a same initial concentration in metal cation (5.10^{-4}M), the quantity adsorbed iron is greater than that of the copper on each of the materials studied, as shown in the table below.

	Pyrophyllite	Pyrophyllite-APMDS
Fe(III)	54%	90%
Cu(II)	0,4%	11,6%

Table 4 Adsorption rate of Fe(III) and Cu(II) on pyrophyllite and pyrophyllite-APMDS.

Differentiation in the adsorption rates of these metals can be attributed to their different characteristics. The tendency of the cations to attach themselves to the surface of the clays involves two factors: the valence of the cation and its hydrated radius. The higher the valency of the cation and the stronger the affinity. Thus, the strong adsorption of the Fe(III) in comparison with that of the Cu(II) is due to its high valence. The same results have been observed by M. Erdemoglu et al [21] in a comparative study of the adsorption of heavy metals on a Turkish pyrophyllite.

VI. CONCLUSION

Within this study we are interested in the adsorption of the Fe(III) and Cu(II) on pyrophyllite and pyrophyllite-APMDS. We recapitulate the main results obtained as follows -The adsorption of Fe(III) and Cu(II) mainly depends on the pH of the solution. Thus, the maximum removal of ions Fe(III) by adsorption on our materials is observed at pH 3.5, knowing that its strong elimination beyond this pH is probably due to its precipitation in the form of hydroxide of iron $\text{Fe}(\text{OH})_3$. For copper, we can note that the maximum removal of Cu(II) ions by adsorption on materials is observed at pH 5.5, knowing that its strong elimination beyond this pH is probably due to its precipitation as the hydroxide $\text{Cu}(\text{OH})_2$. -The effect of the initial concentration shows that: The rate of removal of these ions of iron has been much more important in the case of the pyrophyllite-APMDS in comparison with that of natural pyrophyllite. Thus, for an iron concentration of 5.10^{-4}M , a rate of 90% removal of Fe(III) has been observed in the case of the pyrophyllite-APMDS and 54% for the natural pyrophyllite. For a copper concentration of 5.10^{-4}M , the 60% removal rate of Cu (II) in the case of pyrophyllite-APMDS and a rate of 18% for natural pyrophyllite. Thus, the rate of removal of Cu (II) ions was much higher in the case of pyrophyllite-APMDS compared to that of the natural material. -The kinetic study of iron (III) adsorption of Cu (II) showed that the adsorption equilibrium of iron is reached after the first 30 minutes for pyrophyllite, whereas for pyrophyllite-APMDS the balance is faster as it is reached after 15 minutes of contact. By contrast, the kinetic study of adsorption of Cu(II) revealed that it is relatively slow in comparison with those of the iron as the balance is reached only after 60 min of contact. -The pulp density acts on the removal of Fe (III) and Cu (II),

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since the percentage of adsorption increases by increasing the quantity of the adsorbent, which was explained previously by the availability of active sites in the addition of the material, this phenomenon ends with the establishment of a plateau which corresponds to the adsorption of all the iron and copper present in solution. -Finally, the strong adsorption of the Fe(III) in comparison with that of the Cu(II) is due to its high valence.

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