*Algerian Journal of Environmental Science and Technology*
*Avril edition. Vol.1. N°2. (2015)*
*ISSN : 2437-1114*
*www.aljest.webs.com*

# Adsorption of Copper (II) from Aqueous Solutions on Antimony Pillar/Clay Composite

H. Cherifi, S. Bougherara, K. Louhab

Research Laboratory of Food Technology, Faculty of Engineering Sciences, University of Boumerdes, Boumerdes 35000, Algeria

*Corresponding author: cherifi1ch@gmail

## ARTICLE INFO

***Article History:***

*Received* ***: 21/06/2015***
*Accepted* ***: 09/07/2015***

***Key Words:***
*pillared clays, synthesis, characterization, Antimony, kinetics, Adsorption, ion copper*

## ABSTRACT

*The separation of copper from aqueous systems is studied for environmental protection. In this paper was studied the elimination of cooper from dilute aqueous solution by adsorption on a crude and chemical modified clays (pillared layers clays).The kinetics study of the adsorption of copper on the modified clay showed that equilibrium is reached after 60 mn. A high adsorption performance was recorded for the following optimum conditions at the temperature T = 25°C and the solid/liquid ratio = 2, Initial concentration of ion $Cu^{2+}$ =40 mg /L, the amount of adsorbent clay = 800 mg, pH = 6.*

## I. Introduction

Organic dyestuffs and heavy metals wastewater are currently a major problem for environmental managers [1, 2]. Many different treatment techniques including biological treatment, coagulation, floatation and nanofiltration have been used in in the removal of heavy metals from wastewater [3, 4]. Adsorption is one of the effective methods with the advantages of high treatment efficiency to treated water [4,5].Because of high cost of activated carbon, natural and modified clay, especially montmorillonite, are being widely considered as alternative low cost adsorbents[6,7]. The intercalation of iron and antimony in the materials may provide clays better retain pollutants divalent metal cations such as $Cu^{2+}$, $Cd^{2+}$, $Pb^{2+}$ [8,9]. The Sb-nanoparticles intercalated into the montmorillonite interlayers, which formed Sb-PILCs, has a high specific surface area and basal spacing, it is expected to own a stronger PILC structure than the PILCs synthesized through ion exchange method [10, 11].

We study in this work, synthesis and characterization of modified clay materials used as adsorbents for the removal of copper dissolved in an aqueous solutions.

## II.. Materials and Methods

### II.1. Preparation of Sb-pillared clay synthesis

The polycation solution of Antimony **is** prepared by the polymerization reaction of the $Sb^{3+}$ ion**.** In this synthesis, we proceed to the titration of a solution of 0.4 M antimony chloride ($SbCl_3$, Prolabo) with a basic solution to 0.72 M (NaOH, Fluka). Titration is carried out by means of a funnel drips.We followed daily monitoring of pH and color of the pillaring solution according aging time. Thereafter, the pillaring solution was added drop wise to about 10 g of a clay in 50 ml suspension, for one hour homogenized well are titrated by drop wise pillared solutions of antimony in agitation (500 rpm / min) until mechanical homogenization. The mixture was then dialyzed for 4 days with distilled water once a day is renewed. Drying is performed at 110 ° C; the powder was calcined at 500 ° C, for 3 hours in a muffle furnace. The resulting product is Antimony Pillared clay Mineral (Sb-**PILCs).**

### II.2. Characterization of Sb-Pillared and natural clay Samples

Powder X-Ray Diffraction pattern were recorded on an automatic diffract meter anticathode excited copper under voltage 40 KV, Philips brand, the sample is prepared according to the method of pasta oriented in the clay phase. The Physic-chemical properties of the raw and modified clays were determined by the following techniques: The Specific Surface area ($S_{BET}$) and Average pore Diameter (Dm) by the BET method, density (ρ) by the pycnometer method. For the determination of copper, the apparatus used is an atomic absorption spectrophotometer double beam Perkin Elmer 1100B brand category. The pH measurement is made with a digital pH meter, Ref: pH 212 HANNA laboratories equipped with a combined electrode.

### II.3. Adsorption experimental procedure

We prepared a stock solution of 1000 mg/L of $Cu^{2+}$ in distilled water using copper sulphate ($CuSO_4$ $5H_2O$). The adsorption experiments, using Sb-pillared and natural clay materials, were performed according to the following operating conditions: the volume of the aqueous solution is 400 ml, the temperature is 25 ° C, agitation rate is 200 rev/min and the solid/liquid ratio = 2, pH= 6. Adsorption test was conducted in a static reactor with continuous stirring and by contacting 400 ml of a copper solution with increasing doses of natural and modified clays. Initial pH value was adjusted to (2, 3, 4, 5, 6, 7, 8 and 9) with 0.1M HCl or 0.1M NaOH and the Samples over time and the determination of $Cu^{2+}$ ions are used to monitor the kinetics of adsorption of copper on the bentonite. During our tests, different reaction parameters were varied: the influence of the stirring time, the dose of modified and natural clays, the initial content of $Cu^{2+}$ (20, 30 and 40 mg/L).

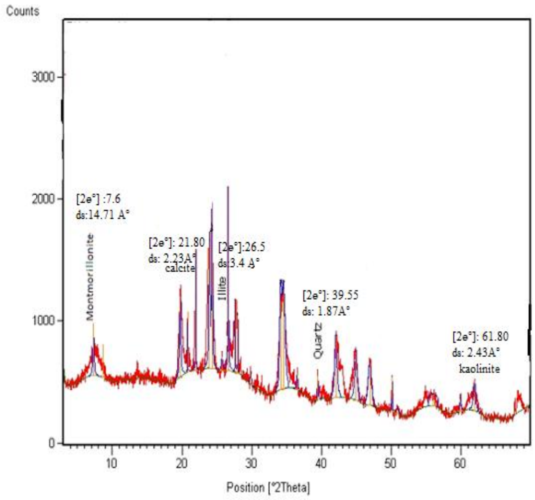
## III. Results and discussion

### III.1. Determination of the mineralogical composition of the crude clay

***Table 1:*** *Mineralogical Composition of the Natural bentonite*

| Natural bentonite | | Mineralogical analysis |
|---|---|---|
| 2ɵ(°) | $d_{001}$(A°) | |
| 7.6 | 14.71 | Montmorillonite |
| 39.55 | 1.87 | Quartz |
| 21.80 | 2.23 | Calcite |
| 26.5 | 3.4 | Illite |
| 61.80 | 2.43 | Kaolinite |

***Fig 1****: XRD Pattern of the Natural Bentonite*




Results of X-ray diffractogram (Figure 1) and Table 1; shows the characteristic lines of montmorillonite, smectite, illite, kaolinite, calcite and quartz. The XRD pattern of the blade oriented air confirms that the natural clay is a smectite- illite interstratified predominantly smectite containing kaolinite, calcite and quartz as impurities.

It should be pointed that clay, contains an important montmorillonitic fraction, generally lends itself to chemical modification which leads to their increased surface area and surface acidity [1, 5].

### III.2. Specific Surface area, pore diameter, Density measurements of the clay samples

Analysis of physical properties of the raw and modified clay materials are shown in table 2, showing an improvement in the porosity of the Sb-pillared material compared with the raw material, which shows an increase in the interlamellar spaces and improving of the porous texture of the material studied. The calcination at 500 °C of the intercalated clay actually increases the specific surface area following the destruction of organic matter. The pore diameter and the volume mass of the pillared bentonite are significantly higher than that of the Natural sample due to the presence of the microporous texture created by the antimony pillars in the interlayer regions. The average pore diameter is within the range typical of smectite clays.

*Algerian Journal of Environmental Science and Technology*
*Avril edition. Vol.1. N°2. (2015)*
*ISSN : 2437-1114*
*www.aljest.webs.com*

***Table 2:*** *Results of Specific Surface area, pore diameter and density of natural and Sb-pillared bentonites.*

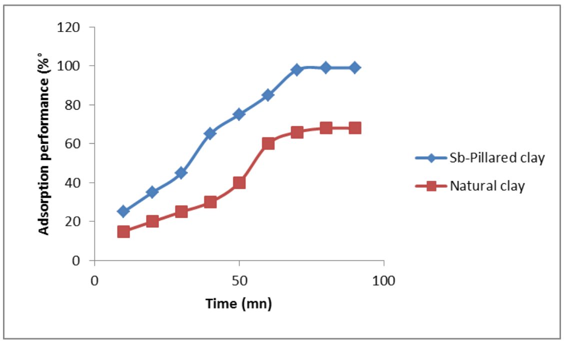
| ***Samples*** | ***Natural bentonite*** | ***Sb-pillared bentonite (calcined at 500°c*** |
|---|---|---|
| **Specific Surface Area ($S_{BET}$, $m^2/g$)** | 68.25 | 365.11 |
| **Pore Diameter (Dm, A°)** | 47.60 | 88.80 |
| **Volume Mass (ρ, g /$cm^{-3}$)** | 2.34 | 2.99 |
| **The interlayer Space (A°)** | 14.47 | 30.05 |

## III.3. Study of the adsorption of copper on clay adsorbents

### III.3.1. Adsorption kinetics

The study of the kinetics of adsorption of metal ions ($Cu^{2+}$) in the solution on the Sb-Pillared and natural clay materials in the following operating conditions: the metal ion concentration is 40mg/l, the volume of the aqueous solution is 400 ml, the temperature is 25 °C, the stirring speed was 200 rev/mn and the solid/liquid ratio = 2, pH = 6. The Fixing Copper $Cu^{2+}$ increases over time, it is rapid for the first 60 min. According to the shape of the curve of the Figure 2, shows the equilibrium saturation acquired from the surface of the clay adsorbents is reached after 60 min.

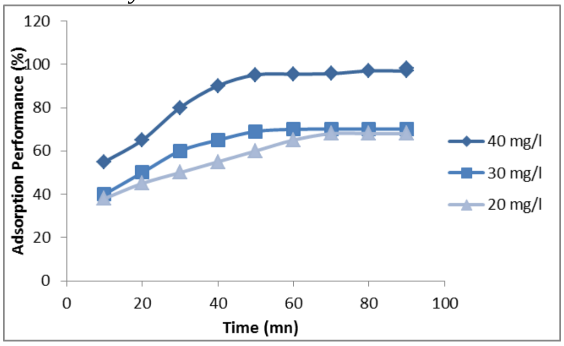
***Fig 2****: Variation of the adsorption rate in function of stirring time, [$Cu^{2+}$] =40 mg/L, T=25°c, pH=6, Adsorbents: Sb-Pillared clay and Natural clay.*




### III.3.2. Effect of initial concentration

The initial concentration of the solution is one of the most important parameters affecting the ion exchange system or adsorption [2, 3]. From the results of the figure 3, it appears that the adsorption rate increases rapidly with time during the first 40 minutes, then it is the saturation of the surface of the clay adsorbents after 60 minutes. An optimal concentration in the adsorption conditions is 40 mg/L copper, the adsorbent mass is 800 mg and the pH = 6.

***Fig 3****: The variation of the adsorption performance in function of stirring time for different initial concentrations, T = 25 ° C, pH = 6, Adsorbent: Sb-Pillared clay*

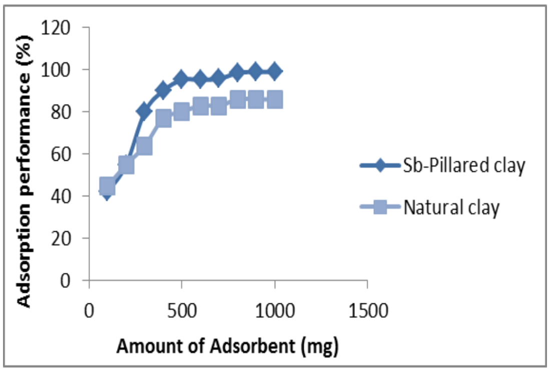



.

### III.3.3. Effect of quantity of Clay adsorbents

The effect of the quantity of adsorbent is used to determine the amount of modified clay necessary to set the maximum adsorption of cooper $Cu^{2+}$. The experimental curve of Figure 4 appears to be linear. For a complete adsorption it is necessary to increase the quantity of adsorbent and therefore a high adsorption performance for an optimal adsorbent mass of 800 mg to a pH=6.The synthetic wastewater was analyzed before and after adsorption.

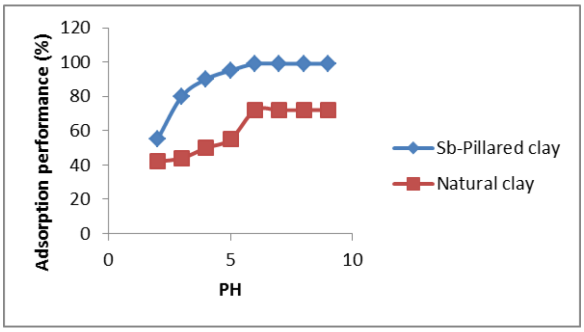
***Fig 4****: The variation of the adsorption performance depending on the amount of adsorbent for both clay adsorbents, [$Cu^{2+}$] = 40 mg/L, T = 25 ° C, pH = 6.*




### III.3.4. Effect of pH

In view of the above results, one can conclude that the pH may be a basic parameter for the progress of the reaction of the copper binding bentonite. The pH is adjusted in a range of 2 to 9 and is kept constant during the first 60 minutes of stirring by adding NaOH (0.1 M) or HCl (0.1M). In Figure 5, we present the adsorption changing with pH to give different yields. The best yields are obtained from a pH of 6 for both clay adsorbents.

***Fig 5**: Effect of pH on the efficiency of Copper removal by adsorption on each Adsorbent, mass: 800 mg, [$Cu^{2+}$] 40 mg / L, T = 25 ° C.*




## IV.Conclusion

This work led to the Algerian clay removing Cu (II) ions from aqueous solution. In the preparation process of the pillaring solution, the important factors that support the main polymerization of the metal ion Sb (III) were studied. These factors are the concentration of metal ion, the molar ratio OH/ Me, the time to maturation of pillaring solution and the agitation speed. The characterization results of this study show that the Sb-pillared bentonite has a high thermal stability and high specific surface area. We managed to prepare Sb-PILCs clay material with basal spacing ranging from 30.057 A° depending on the nature of the intercalated polycation complex. The textural analysis by the XRD and BET method of the Sb-Pillared bentonite allowed us to confirm the creation of a dense microporous network compared to the natural clay, caused by the intercalation of large metal pillars. With the properties determined, Sb-Pillared bentonite clay is highly reactive matrice which can be used in decontamination processes of industrial wastewater. In testing the efficacy of the clay materials for retention copper, various reaction parameters were studied; the kinetic study of the adsorption of copper showed that equilibrium is reached after 60 minutes. A high adsorption performance was recorded for the following optimum conditions at the temperature T = 25 °C and the ratio solid/liquid = 2: Initial concentration of ion $Cu^{2+}$ = 40 mg/l, the amount of adsorbent clay = 800 mg, pH = 6.

## V. References

1. A. Boukerroui, A. Ourari, M. Said Ouali, Copper (II) ions removal from aqueous Solution using bentonite treated with ammonium chloride. American journal of Physical Chemistry. Vol. 1(1):1-10, 2012.
2. Shankar.Naik Maya, Sivapullaiah P.V, Syed Abu Sayeed Mohammed, Sorption of Iron and Copper on Sand Bentonite Fly ash Mixtures. International journal of Research in chemistry and Environment.Vol.4 (2), 1-8, 2014.
3. E.Eren, B Afsin, Removal of copper (IIBy adsorption on a gross and activated bentonites; Combined potentiometry, Thermodynamics, XRD,
4. IR, ATD, Journal Hazardous Materials. Vol. 51(2-3), 682-691, 2008.
5. Wong Chee Sien, Nurul Aimi biniti Rohaizar, Removal of Cu (ll) from Water by Adsorption on Chicken Eggshell. International Journal of Engineering and Techology.Vol:13(1), 1392-4646, 2013.
6. T. Chouhane, S. Chouchane, A.Boukari. Elimination du Manganèse en solution par le Kaolin: Etude Cinétique et thermodynamique. Revue des Energies Renouvelables. Vol.16 (2), 313-335, 2013.
7. R. Sabreen Alfarra; N.Eman Ali, Mashita Mohd Yusoff, Removal of heavy metals by natural adsorbent; International Journal of Biosciences.Vol.4, N°. 7,130-139, 2014.
8. L.Cottet, CAP Almeida, N.Naidek, MF Viante, MC Lopez, NA Debacher.The adsorption characteristics of montmorillonite clay modified with iron oxide relative to the methylene blue in an aqueous medium. Applied Clay Science.Vol.95, 25-31, 2014.
9. Fen. Rao, Shaoxin. Son, Lopez Valdiviesco, Synthesis and Characterization of Ag-PILC through the formation of Ag@Montmorillonite Nano composite. Nano: Brief and review. Vol.10.N°.2, 1550031, 2015.
10. Verma Poonam, Chaudhary Pratibha and Kumar Atul; Removal of Reactive Orange 107 Dye from Textile Effluent by Adsorption on Acid Treated Fly Ash. Research Journal of Chemistry and Environment. Vol.18 (11), 2014.
11. Gannouni, H Ben Amor, M Chlendi; Study of Adsorption ions $Zn^{2+}$ in aqueous Solution on natural clay. Annals of Chemistry –
12. Materials Sciences. 35/4, 235-248, 2010.
13. A.Bennani, M. Badia, M .Hachkar, M. Bakasse. Basic elimination of the dye Methylene blue from aqueous solution With the Clay of SAFI. Journal of Water Science 23 (4), 2010, 375-388.
14. D.I Nistor, N. D Miron, A Azzouz, Kinetics Retention of Radioactive Elements On the pillared clays originally Romanian, Scientific Study and Research, 2(3), 5409, 2006.
15. M. Eloussaief, M. Benzina, Efficacity of Natural and Activated Clay by an acid for the removal of Pb (II) from Aqueous Solutions, Journal of Hazardous Materials, 178(1-3), 753-757, 2010.
16. D.Alemayehu, S.K.Singh and D.A.Tesse, Assessment of The Adsorption Capacities of Fired Clay Soils from Jimma (Ethiopia)
17. For the Removal of Cr (VI) From Aqueous Solution,Universal Journal of Environmental Research and Technology, 2(5), 411-420, 2012.
18. A.Gannouni, A. Bellagui, M. Bagane, Activation of Clay For bleaching olive Oil. Annals Of Chemistry, Materials Science,
19. 1999, 24(6), 407-416.
20. S.Elbaridji, M. Elamine, H. Eljazouli, Treatment and Recovery Of Sub-wood products, Application to The disposal of industrial dyes, Account Rendered Chemistry, 2006, 9(10)1314-1312.
21. N. Boualla, FH Saad,B. Hadj Hassan ,Z.Derrich and A. Benzian, Kinetics of Elimination of dye methylene blue By activated sludge, Liberty Science, 4(120305), 2111-4706, 2012.
22. S. Caillere, S. Henin, Mineralogy Of Clays. Masson and Cie.1983.

23. Z. Dali-Yousef, H. Bouabdasselem, Removal of Organic Compounds by Local Clays, Account Rendered Chemistry, 9(10), 1295-1300, 2006

**Please cite this Article as:**
Cherifi, H., Boughrara, S., Louhab, K., Adsorption of Copper (II) from Aqueous Solutions on Antimony Pillar/Clay Composite, ***Algerian J. Env. Sc. Technology***, **1:2 (2015) 14-18**