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

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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 pores Diameter ($D_m$) by the BET method, density ($\rho$) 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$_2$O). 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

<table>
<thead>
<tr>
<th>Natural bentonite</th>
<th>Mineralogical analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ(°)</td>
<td>d$_{001}$(Å)</td>
</tr>
<tr>
<td>7.6</td>
<td>14.71</td>
</tr>
<tr>
<td>39.55</td>
<td>1.87</td>
</tr>
<tr>
<td>21.80</td>
<td>2.23</td>
</tr>
<tr>
<td>26.5</td>
<td>3.4</td>
</tr>
<tr>
<td>61.80</td>
<td>2.43</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Samples</th>
<th>Natural bentonite</th>
<th>Sb-pillared bentonite (calcined at 500°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Surface Area (SBET, m²/g)</td>
<td>68.25</td>
<td>365.11</td>
</tr>
<tr>
<td>Pore Diameter (Dm, Å)</td>
<td>47.60</td>
<td>88.80</td>
</tr>
<tr>
<td>Volume Mass (ρ, g/cm³)</td>
<td>2.34</td>
<td>2.99</td>
</tr>
<tr>
<td>The interlayer Space (A°)</td>
<td>14.47</td>
<td>30.05</td>
</tr>
</tbody>
</table>

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 (Cu²⁺) 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 Cu²⁺ 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, [Cu²⁺] =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 Cu²⁺. 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, [Cu²⁺] = 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 Å 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 matrix 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**

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