STUDY OF COPPER ION ADSORPTION FROM AQUEOUS SOLUTION BY NATURAL PALYGORSKITE (ATTAPULGITE)

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ABSTRACT

In the current study the possible application of palygorskite clay (mined from Ventzio area, Grevena, Greece) as a sorbent for Copper metal ions from aqueous solutions was evaluated.

The clay sample was evaluated a) as received, b) after being washed with water and c) after being treated with HNO_3. Dynamic measurements were performed to investigate the rate of adsorption of copper ions, as well as the total adsorption capacity in different temperatures, pH conditions and clay's particle sizes. The adsorbents were characterized by Cation Exchange Capacity (C.E.C.), and nitrogen porosimetry which determined the surface area and total volume of pores before and after the treatment. Overall it was observed that the solution's pH was the dominant factor while treatment of palygorskite did not present better adsorption results in comparison to natural palygorskite.

INTRODUCTION

Since the industrial revolution, waste from many industries like electroplating, metallurgical, leather production, chemical and battery manufacturing industries, is discharged into the environment containing various heavy metals. The existence of heavy metals in the aquatic system is well known to be very harmful for all living species and received considerable attention in recent years due to the primarily concern that heavy metals practically do not biodegrade and they can be readily be absorbed by animals and enter directly human's food chain. As a result, they tend to accumulate in living organisms in high concentrations, thus presenting a high health risk to consumers and causing several health problems.

A number of technologies for the removal of metal ions from aqueous solutions have been developed over the years. However, all these technologies have limitations and/or are unable to achieve the standards set by international water association bodies [1]. In order to minimize processing costs, several technologies have focused on the use of low cost adsorbents, e.g. agricultural by-products [2], waste materials [3], bio-sorbents [4,5,6] and clay materials [7]. Clay is readily available, inexpensive material and offers a cost-effective alternative to conventional treatment of the aforementioned waste streams [8]. Palygorskite, also known as attapulgite, is one of these low-cost materials. It is a hydrated magnesium aluminum silicate hydroxide with the theoretical formula: $Mg_5(Si,Al)_8O_{20}(OH)_2(OH_2)_4\cdot 4H_2O$ and it has been found to have the ability remove heavy metals (Pb^{2+}, Ni^{2+}, Cu^{2+}) from aqueous solutions [9].

MATERIALS AND METHODS

- **Materials and preparation of solutions and samples**

A palygorskite sample, brown in colour, examined on three particle sizes **Coarse** (16/60mesh), **Medium** (30/60mesh) and **Fine** (<100μm), donated from GEOHELLAS S.A. (located in Grevena).

The adsorbent was evaluated as follows:

- Without any treatment (**natural**)
- After being washed (four times with deionized water for 15-20 min each time) (**washed**)
- After treated according to Al-Degs et.al.2006 [10] (**acid-treated**) as follows:
  30 g sample of dried clay was added to 625 ml distilled water. The mixture was heated to 90 ^oC for 2 hours under continuous stirring while 625 ml of 0.1M HNO_3 was gradually added to the clay solution. In the end, the palygorskite was completely washed 4 times with deionized water under continuous stirring.

Before any experiment, the palygorskite was placed in incubator for over 12 hours in 135-140^oC, so the samples were dry in order for any humidity to be removed. The pH value of the Cu^{2+} ions solutions were always measured before any experiment and were adjusted with the corresponding quantity addendum of reagents, (HCl 0,1M and NaOH 0,1M). The change of solution's pH, would affect the concentration of copper ions, so it took place before the adjustment of the concentrations. A stock Cu^{2+} solution (1000 mg/L) made by dissolving $CuSO_4{\cdot}5H_2O$ in ultrapure water, and used as a bases for all experiments, which was further diluted to the desired concentrations (5 mg/L). The measurement of Cu^{2+} concentration was performed on a Lovibond SpectroDirect spectrophotometer. Specifically, for the determination of the concentration of Cu^{+2}, bikinotinic or dicinonic acid (bisconic acid, Bicinchoninate), 2,2'-biquinoline-4,4'dicarboxylic acid were used, which is a weak acid and consists of two rings carboxylated quinoline.

Prior any measurement on the spectrophotometer, it was very important that the samples were transparent, therefore, 20 ml from the samples' taken for centrifugation (Universal 320) in 9000 rpm for 20 minutes.

- **Materials Characterization**

Nitrogen Porosimetry and Cation Exchange Capacity (C.E.C), were performed for the characterization of palygorskite in order to determine specific surface area, total pore volume and the pore size distribution of the Palygorskite before and after acid treatment.

The ability of clays to hold and exchange cations is characterized as Cation Exchange Capacity [11].For the determination of Cation Exchange Capacity the Jackson Method was used (1998) [12]. This method is based on changes in the pH of a standard solution of 1 M acetic acid. According to the method, 2.5g of material were placed in a 50 ml beaker with the addition of 25 ml of acetic acid and stirred for one hour on a mechanical stirrer. After stirring, the mixture was left so that any large particles settle. CEC results from the following equation:

$$\mathbf{CEC / M = (observed\ pH - pH\ acetic\ acid) \times 22} \qquad (1)$$

where CEC = mmol kg^{-1} cations while M equals 0.1 kg of material.

N_2 porosimetry at 77 K was used to two samples of natural Palygorskite and to two acid treated in different particle size to examine the effects of the modification (**medium-natural**, **Fine-natural**, **medium/acid-treated** and **Fine/acid-treated)**. The measurements were made in a Quantachrome Autosorb-1, porosimeter. The experimental process initially involves placing the samples in suitable glass cells and then degassing them at the respective stations, under high vacuum (10^{-5} $Torr$) and temperature of 350^oC for 24-48 hours.

Batch adsorption experiments

The removal of Cu^{2+} in adsorption experiments was studied as a function of pH, contact time, particle size of clay, temperature and treatment.

- **5 mg/L Cu^{2+} adsorption experiments**

Adsorption experiments were carried out in 200 mL flasks adding 0.1 g of adsorbent into 100 mL of copper solution, in concentration of 5 mg/L and shaking in a thermostatic shaker bath (Julabo SW22) set at 200 rpm for totally 75 min according to similar studies. In the beginning, adsorption processes were observed to be rapid and equilibrium followed by slow sorption and was achieved after approximately 75 min. Furthermore, according to other studies, the adsorption took place in 3 different temperatures 15°C, 25°C and 35°C, as well as in 3 different pHs 3, 5, and 8,5. The Cu^{2+} adsorption test at pH> 8.5 resulted in copper precipitation something that was anticipated and even extensively mentioned in the user manual of the instrument used (Lovibond SpectroDirect). Respective phenomena also occur at pH lower than 3. The adsorption capacity of Cu^{2+} was calculated using the following Eq(2):

$$q_m = \frac{(\mathrm{Cin}-\mathrm{Cf})}{\mathrm{m}} \mathrm{V} \qquad (2)$$

where q_m (mg/g) is adsorption capacity of Cu^{2+} at the time t (q_t, mg/g), V is the solution's volume (L), C_{in} and C_f are initial and final Cu^{2+} concentration (mg/L) and m is total mass of adsorbent used (g). At the desired time, the supernatants were decanted as already mentioned for centrifugation (20ml), until clear and then their concentration measured with the spectrophotometer.

- **Total adsorption capacity determination**

Total adsorption capacity is defined as the adsorbed amount of ions per sorbent mass (mg/g) in equilibrium, namely in infinity time. As final time point of equilibrium is defined the time when no change in adsorption values is observed. This time for the entire set of experiments was determined at approximately 100 hours. For practical reasons, the final concentration of Cu^{2+} in the supernatant solution ought to be detectable from the spectrophotometer (>0.05 mg/L). According to the above, the mass of the absorbent was determined in 0,031g. The experiments were done twice and the results were averaged.

RESULTS AND DISCUSSION

- **Nitrogen adsorption at 77K**

Total pore volume, specific surface area and pore size distribution characteristics were determined by using nitrogen adsorption measurements at 77K. The shape of the adsorption isotherm (type II with H4 hysteresis loop) was similar for all the studied samples. In **Fig1** are presented the N_2 isotherms at 77K for the two of the studied palygorskite clay samples. The total pore volume for the four measured samples is fluctuated from 210 to 270cc/g (STP), with a specific surface area in the range of 180 to 225 m^2/g. An increase in the surface area up to 25% for the sample after modification treatment was recorded. For all four samples the average pore size was estimated to 5nm (**Table1**).

Table 1. *Characteristics of porous structure of Palygorskite.*

Sample	Total pore volume (cc/g) STP	Surface area, BET, (m^2/g)	Pore size distribution (nm)
MEDIUM/NATURAL	220	180	5
FINE/NATURAL	270	190	5
MEDIUM/ACID-TREATED	235	225	5
COARSE/ACID-TREATED	210	200	5

Also, the total pore volume differed slightly 220cc/gr (STP) to 232cc/gr (STP) (**Fig1**). This demonstrated that areas within the porous network which were characterized by particular constrictions were broken through processing with HNO_3, increasing the total pore volume and surface area.

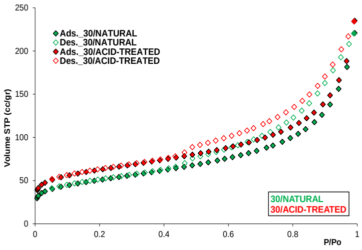

Fig 1. *Isotherm adsorption/desorption N_2 to 77K.*

In the case of Fine/Natural sample the total pore volume was larger than the Coarse/acid-treated. This can be attributed to the fact that the natural sample has areas which are collapsed after the acid treatment by resulting to the smaller effective pore volume.

Pore size distribution was determined based on the approach FMS equation [13]. As it is shown the pore size was the same before and after the acid-treatment, for all the studied samples, something which confirms that the cleaning process with acidic aqueous solution wasn’t enough to rupture pores and to create a porous network of larger dimensions than natural mineral.

- **Cation Exchange Capacity (C.E.C.)**

According to the Table1, there is no substantial difference between the natural and washed palygorskite, on both particle sizes. As for acid-treated samples, there is a significant difference in C.E.C. and in specifically between the smaller particle sizes, which indicates that the acid treatment either reduced or covered the potential positions that the cations could occupy. The results are also consistent with porosimetry results.

Table 1. *Results of C.E.C.*

Sample	**C.E.C. (meq/100g)**
Coarse-natural	14,96
Coarse-washed	16,72
Coarse-acid treated	6,16
Medium-natural	15,84
Medium-washed	16,28
Medium-acid treated	5,06

- **Adsorption Kinetics**

The shaking time (contact time) seems to be very important factor, as expected. There are a lot of studies which mentioned that the rate of Cu^{2+} sorption is faster during the first 20-30 minutes, and then the rate slows down until the equilibrium point [14,9,15,16]. The phenomenon can be explained to the fact that initially the active adsorption positions for Cu^{2+} on the surface of palygorskite are uncovered and in excess [17,15]. As a result, developing stronger interactions between the adsorbed substance and the sorbent. As time passes, the phenomenon is reversed gradually, as more ions are adsorbed on the surface of the sorbent and weak ion-ion affinity forces prevail.

As already mentioned, in the basic environment (pH8,5) from the first 5 minutes, over 80% of the total amounts of copper ions have been adsorbed, This is due to interactions which are affected by the electrostatic attraction between the surface charge and the ions which compete with water ions. [14,9,15].

The acidic environment **(pH3)** seems to slow down the rate of the process independently of temperature, particle size or treatment. (Fig. 2-3).

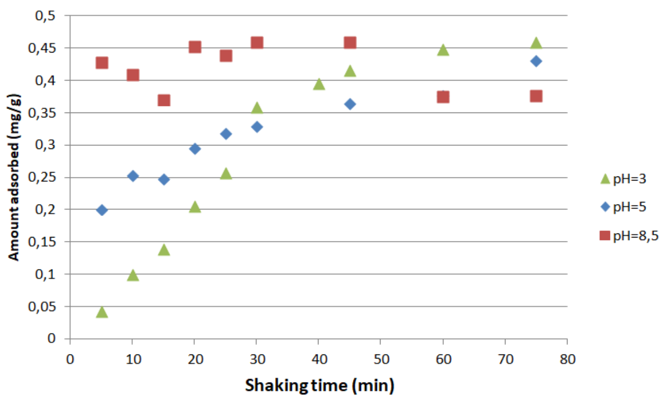

Fig 2. Comparison of the effect of pH (pH=3, 5 & 8,5) of adsorption, to 25°C.

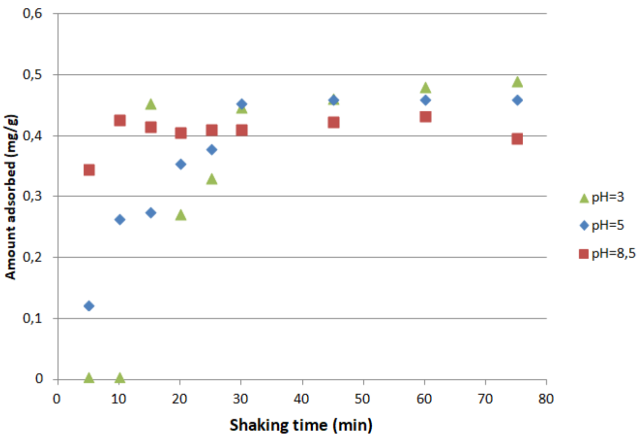

Fig 3. Comparison of the effect of pH (pH=3, 5 & 8,5) of adsorption, to 35 °C

- **Total adsorption capacity**

The results from the Total adsorption capacity shows the importance of the pH. The most favorable conditions were in the basic environment **(pH8,5)** and in 15°C, independently the palygorskite treatment or the initial particle size of clay. As the pH becomes acidic **(pH3)**, the quantity of the total adsorption was lower, especially in 15°C. The differences of the results between particle size and treatment of the palygorskite weren’t noteworthy.

CONCLUSIONS

The sorption of Cu^{2+} on Palygorskite was investigated in the pH range 3–8.5. In summary, regardless of the temperature, particle size, or acid treatment of the material, basic environment favored adsorption. Specifically, in pH 8,5 the higher quantity of the total amount of copper ions have been adsorbed, which is attributed to the absence of proton (H^+) acting as competitors with copper ions (Cu^{2+}).

In acidic environments, there was a decrease in the rate of the adsorption, as well as in the total amount of copper ions adsorbed, but the final equilibriums were generally higher.

The effect of modification on palygorskite specimens with HNO_3 wasn’t significant as the process wasn’t capable to alter the structural characteristics of the material (surface area, pore size distribution and total pore volume).

The results obtained for treated palygorskite were inferior compared with the natural specimens.

The results from Adsorption Kinetics were comparable to other reported works. Specifically, the rate of sorption Cu^{2+} was faster during the first minutes. As the surface activity of the material decreases, decreases as well the pace of the sorption, as a result the adsorption process gets slowed equilibrium point.

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