

## Study of Cu<sup>2+</sup> and dyes removal by sorption onto palygorskite in batch and continuous flow processes

M. Pachoulis<sup>a</sup>, A.A. Sapalidis<sup>a,\*</sup>, E.P. Kouvelos<sup>a</sup>, A. Gotzias<sup>a</sup>, G.Z. Kyzas<sup>b,\*</sup>, E.P. Favvas<sup>a,\*</sup>

<sup>a</sup>Institute Nanoscience and Nanotechnology, National Centre for Scientific Research “Demokritos”, 153 41, Agia Paraskevi, Attica, Greece, emails: a.sapalidis@inn.demokritos.gr (A.A. Sapalidis), e.favvas@inn.demokritos.gr (E.P. Favvas)

<sup>b</sup>Hephaestus Laboratory, Department of Chemistry, Hellenic International University St. Lucas, 654 04, Kavala, Greece, email: kyzas@chem.ihu.gr

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### ABSTRACT

In the current study, the potential use of palygorskite (is also mentioned as “attapulgitite”) clay as a sorbent for copper metal ions and dyes (Methylene blue) from aqueous solutions, which can be both industrial and urban, was examined. The clay sample was evaluated (a) as received without any further modification, (b) after water washing and (c) after acidic treatment (HNO<sub>3</sub>). The adsorbents were characterized by cation exchange capacity, X-ray diffraction and nitrogen porosimetry. Dynamic measurements were performed in order to investigate the effect of different temperatures, pH values and clay’s particle sizes on Cu<sup>2+</sup> adsorption. Breakthrough curves for Cu<sup>2+</sup> and dye were performed in order to resemble real industrial applications. It was observed that the solution’s pH was the dominant factor whereas treatment of palygorskite did not change significant the adsorption results in comparison to raw palygorskite.

**Keywords:** Palygorskite; Adsorption; Breakthrough; Copper ions; Dyes; pH; Treatment; Temperature; Particle size; Cation exchange capacity

### 1. Introduction

From the years of the industrial revolution and beyond, wastes from various industrial processes such as metallurgical, leather production, electroplating, battery and chemical manufacturing are dumped into the environment with many of them containing large amounts of heavy metals. It is well known that the existence of heavy metals in the aquatic system it is very harmful for all living species. It also has received considerable attention, mainly in recent years, because of the primarily concern that heavy metals practically do not biodegrade and as a result, they tend to accumulate in living organisms in high concentrations (bioaccumulation). Thus, this fact is

presenting a potential high health risks to consumers and causing several health problems in the living organisms.

In order to provide solutions for the removal of metal ions from aqueous solutions a large number of effective technologies 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]. To this end, and in order to minimize processing costs, several technologies have focused on the use of low-cost adsorbents, that is, agricultural by-products [2,3], waste materials [4], bio-sorbents [5–7] and clays [8]. Clay material is a readily available, inexpensive material and offers a cost-effective alternative to conventional treatment of the aforementioned waste streams [9]. Palygorskite

\*Corresponding authors.

clay material, also known as attapulgite, is classified in the list of the low-cost materials. It is a hydrated magnesium aluminum silicate hydroxide substance with the chemical formula:  $Mg_5(Si,Al)_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ . Palygorskite has the ability to remove heavy metals ( $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Cr^{VI}$ ) and also dyes from aqueous solutions through the physical adsorption mechanism [10].

## 2. Materials and methods

### 2.1. Materials and preparation of solutions and samples

Palygorskite samples, brown in color, were examined on three different particle sizes: (i) coarse (16/60 mesh: 250–1,180  $\mu m$ ), (ii) medium (30/60 mesh: 250–600  $\mu m$ ), and (iii) fine (<100  $\mu m$ ), which were kindly provided from GEOHELLAS S.A. (located in Grevena City, North-Western Greece).

The palygorskite was evaluated as follows:

- Without any modification (raw),
- After rinsing (after rinsing with deionized water for 20 min each time) (washed),
- After treated, according to Al-Degs et al. [11] with  $HNO_3$  (acid-treated), as follows: 30 g of the dried clay sample was added into 625 mL of distilled water. The suspension was heated up to 90°C for 2 h under continuous stirring, whereas 625 mL of 0.1 M  $HNO_3$  was gradually added to the clay solution. At the end, the palygorskite was completely washed 4 times with deionized water under continuous stirring. The charge of the materials' treatment was decided based on the nature of the target pollutant. Given that the target pollutants were positively charged (copper ions and Methylene blue dye (it has clear positive charge)), the modification of the materials was decided to be with acid in order to increase the acidic nature of the material

Before each adsorption experiment, preparation of the palygorskite sample was performed by placing an adequate amount in incubator for over 12 h at 140°C, in order to remove the absorbed humidity. The pH value of the  $Cu^{2+}$  ion solution was measured before each experiment and was adjusted with the appropriate micro-addition of acid or alkali (HCl 0.1 M and NaOH 0.1 M). A stock  $Cu^{2+}$  solution (5 mg/L) was prepared by dissolving  $CuSO_4 \cdot 5H_2O$  in deionized/ultra-pure water, and was used as the basis for any afterbirth experiment. The measurement of  $Cu^{2+}$  concentration took place on a Lovibond SpectroDirect Spectrophotometer by using 2,2'-Biquinoline-4,4'-dicarboxylic acid reagent.

Prior any measurement on the spectrophotometer, and in order to remove any suspended solids, 20 mL from the aqueous samples were centrifuged (UNIVERSAL 320) for 20 min and in 9,000 rpm and the supernatant was used to determine the  $Cu^{2+}$  concentration.

### 2.2. Materials characterization

$N_2$  porosimetry and cation exchange capacity (CEC) measurements were performed for the characterization of palygorskite in order to determine the specific surface area, the total pore volume, the pore-size distribution and the ion

exchange capacity of the palygorskite material before and after treatment.

The property, the ability of clays to hold and exchange cations is mentioned as cation exchange capacity [12] and its determination is an important factor involving several methods using for example radioactive isotopes [13].

The Jackson Method [13] was used in order to determine the cation exchange capacity. The method is based on the estimation of pH for a standard acetic acid solution, and simultaneously, the pH of the supernatant is also measured, and practically this value was the same of this of the mixture solution. According to this method, 2.5 g of material is placed in a 50 mL beaker with the addition of 25 mL of acetic acid and stirred, mechanically, for 1 h. After this process, the mixture was left and the large particles are precipitated. The CEC resulting from the following equation:

$$\frac{CEC}{M} = (\text{Observed pH} - \text{pH acetic acid}) \times 22 \quad (1)$$

where cation exchange capacity (CEC) =  $mmol\ kg^{-1}$  cations and  $M$ , is the mass of material (note that the mass "M" of dry soil or sediment is 1 kg).

Two raw palygorskite samples and to two acid-treated were examined by  $N_2$  adsorption at 77 K in order to determine any effect of the washing/acid treatment (Figs. 1 and 2). A Quantachrome Autosorb-1 Porosimeter was used for these measurements. All studied samples are putted and sealed into glass cells and are outgassed under high vacuum ( $10^{-5}$  Torr) and at temperature of 350°C for 12–24 h.

### 2.3. Copper ions adsorption study

Temperature of solution, pH and contact time, treatment of material and particle size of material was investigated as the function of the  $Cu^{2+}$  removal ability of palygorskite clay.

#### 2.3.1. Batch adsorption experiments

Adsorption experiments (kinetics) took place in 100 mL flasks containing 0.1 g of the adsorbent into 100 mL of copper ion solution (5 mg/L) under stirring, (continuous shaking) in a thermo-controlled shaker-bath (Julabo SW22), at 200 rpm for 75 min, as numerous similar studies reports [1,10,11,14,15]. The adsorption process was observed to be initially rapid, followed by slow rate with the equilibrium plateau achieved after approximately 75 min. Furthermore, the adsorption study was performed in the three temperatures of 15°C, 25°C and 35°C, as well as in three different pH of 3.0, 5.0, and 8.5.  $Cu^{2+}$  adsorption at pH lower than 3 and higher than 8.5 resulted in copper precipitation, as was expected. The adsorbed  $Cu^{2+}$  capacity has been calculated using Eq. (2):

$$q_m = \frac{(C_{in} - C_f)}{m} V \quad (2)$$

where  $q_m$  (mg/g) is the adsorption capacity of  $Cu^{2+}$  at 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 each predefined time, supernatants (20 mL), were decanted for centrifugation and their copper ions concentration was measured spectrophotometrically.

### 2.3.2. Total adsorption capacity determination

The total adsorption capacity is defined, in equilibrium conditions, and it is mentioned as “in infinite time”, as the adsorbed amount of ions per sorbent mass (mg/g). As equilibrium time is defined this time point where after that no any notable change in measured adsorption amount is observed. In our case this time was measured equal to about 100 h. The final concentration of  $\text{Cu}^{2+}$  which was being measured in the supernatant solution it should be detectable from the photometric method ( $>0.05$  mg/L). Based on this, the adsorbent mass was set at 0.031 g. The concentration of the solutions was 5 mg/L of copper solution in 200 mL beaker. The experiments for each parameter (pH, temperature, particle size distribution and treatment of the material) were repeated twice and the results were averaged.

### 2.3.3. Fixed-bed column adsorption

Breakthrough experiments with continuous-flow adsorption were performed according to similar studies [16–18] in a vertically placed of 4 mm in inner diameter glass column and a total length of 7.5 cm. The flow of copper ion solution with concentration of 5 mg/L was pumped in upward-direction with a flow rate of approximately 40 mL/min. The quantity of the adsorbent included in the columns were the same for all breakthrough experiments and weighed approximately 0.7 g of dried palygorskite which was fixed in the glass column using fiberglass mesh at the end caps. At the column's exit, 10 mL effluent samples were collected in specified time intervals, using glass vials.

During the adsorption tests, it was found that the fine particle size sample induced a large pressure drop resulting in very different experimental conditions, therefore the comparison of the dynamic study was done between the medium and coarse particle size samples.

The total amount of adsorbed copper ions  $q_{\text{total}}$  (mg/g) was calculated according to González-López et al. [16]. Total mass of adsorbate is equal to the area beneath the curve of the plot of the adsorbed metal concentration ( $C_{\text{adsorbed}} = C_0 - C$ ), as a function of time  $t$  as shown:

$$q_{\text{total}} = \frac{QC_0}{1,000} \int_0^{t_c} \left(1 - \frac{C}{C_0}\right) dt \quad (3)$$

where  $Q$  is the volumetric flow rate (mL/min),  $C_0$  and  $C$  the initial and final concentrations of copper ions respectively, and  $t$ , duration in minutes. During the breakthrough experiments flow rate and pressure drop across the column were recorded and the corresponding diagrams pressure vs. time were constructed in order to study the behavior of the fixed-bed over time and to avoid pressure build-up.

### 2.3.4. Adsorption modeling for fixed bed column studies

Various simple mathematical models were used to fit the experimental data, understand the dynamic behavior of

the column and allow some coefficients to be evaluated (maximum adsorption capacity, equilibrium time, etc.). Extended Langmuir model or Langmuir EXT1, which is an extended Langmuir adsorption isotherm equation used in this study for fitting and is described by the following equation:

$$Q_i = \frac{b_i q_{m,i}^L C_i}{1 + \sum_{j=1}^N b_j C_j} \quad (4)$$

where  $b$  and  $q_m$ , are related to the affinity and maximum sorption, respectively. The model assumes a monolayer adsorption process on a homogeneous surface and would be most applicable in cases where all binding sites exhibit uniform behaviour towards the sorbate.

where  $Q_i$  is the adsorbed amount of component  $i$ ,  $N$  is the number of components,  $C_j$  ( $j = 1, 2, \dots, n$ ) is the equilibrium concentration for each component, whereas  $b_i$  and  $q_{m,i}^L$  the Langmuir constants.

## 2.4. Methylene blue adsorption study

The removal of the cationic dye, Methylene blue, in adsorption experiments was also studied as a function of contact time and pH, as well as of temperature of solution.

### 2.4.1. Batch adsorption experiments

Adsorption experiments (kinetics) took place in 100 mL flasks containing 0.1 g of the adsorbent into 100 mL of Methylene blue dye solution (5 mg/L) under stirring, (continuous shaking) in a thermo-controlled shaker-bath (Julabo SW22), at 200 rpm for 75 min, as numerous similar studies reports [1,10,11,14,15]. Furthermore, the adsorption study was performed in three temperatures, 15°C, 25°C and 35°C, as well as in three different pH of 3.0, 5.0, and 8.5. The selection of the aforementioned pH values was for comparison reasons, because the adsorption experiment for  $\text{Cu}^{2+}$  removal was carried out at those pH conditions. The dye content of samples after adsorption was measured spectrophotometrically (UV-Vis, Model U-2000, Hitachi) at  $\lambda_{\text{max}}$  of Methylene blue (633 nm).

## 3. Results and discussion

### 3.1. Nitrogen adsorption at 77 K

$\text{N}_2$  adsorption isotherms at 77K were performed in order to determine structural characteristics of the samples, such as pore-size distribution, total pore volume and specific surface area. The three studies present similar, of type II with H4 hysteresis loop, isotherms. Fig. 1 presents the  $\text{N}_2$  isotherms at 77K for the medium raw and medium/acid-treated of the studied palygorskite clay samples.

In Table 1 are summarized the total pore volume (cc/g, STP) and the surface area ( $\text{m}^2/\text{g}$ ) for the nine studied samples. The values for the total pore volume are fluctuated from 200 to 282 cc/g (STP), whereas the calculated specific surface area was recorded between 168 and 240  $\text{m}^2/\text{g}$ . The treatment process resulted in an increase of the surface

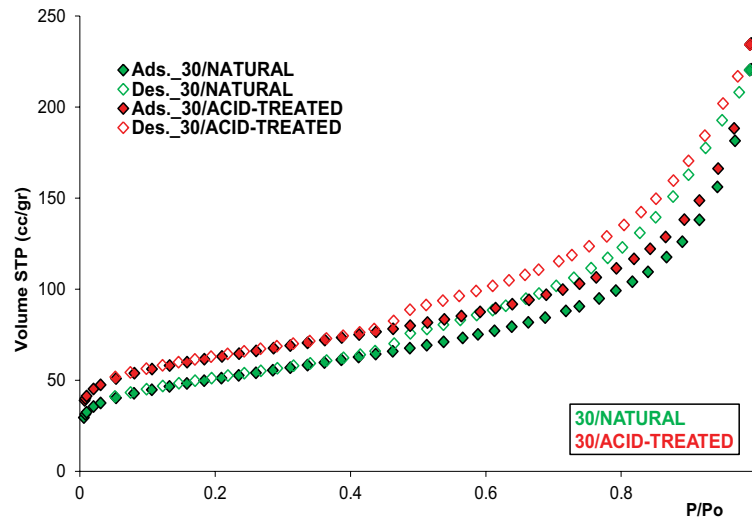


Fig. 1.  $N_2$  adsorption isotherm at 77 K for medium/raw and acid-treated.

Table 1  
Characteristics of porous structure of palygorskite

Sample	Total pore volume (cc/g) STP	Surface area, BET, ( $m^2/g$ )
Fine/raw	$270 \pm 5.4$	$190 \pm 3.4$
Medium/raw	$220 \pm 4.4$	$180 \pm 3.7$
Coarse/raw	$203 \pm 3.6$	$168 \pm 3.5$
Fine/washed	$264 \pm 4.6$	$192 \pm 4.2$
Coarse/washed	$230 \pm 3.3$	$184 \pm 3.2$
Medium/washed	$200 \pm 3.7$	$171 \pm 3.7$
Fine/acid-treated	$282 \pm 4.0$	$240 \pm 4.5$
Medium/acid-treated	$235 \pm 3.9$	$225 \pm 4.1$
Coarse/acid-treated	$210 \pm 4.2$	$200 \pm 4.8$

area up to 18%, but the average pore size was calculated of about 5 nm for all studied samples.

Also, the total pore volume differed slightly after modification 200 cc/g (STP) to 240 cc/g (STP) (Fig. 1). This increase of the pore volume and surface area, after treatment, can be attributed to the removal of impurities and constrictions, mainly in blind pores' entrances.

FMS [19] Eq. (5), was used for the determination of the pore size. The calculated pore size was almost the same before and after the acid-treatment, for all the studied samples, in the range of about 5 nm.

$$r_p \left( \text{\AA} \right) = \frac{r_k}{0.72} + 7.2 \quad (5)$$

where  $r_k$  is the Kelvin radius.

### 3.2. Cation exchange capacity

Jackson Method [13] was used for the determination of cation exchange capacity. As it is obvious in the Table 2 the particle size of the sample didn't effect crucial on the

Table 2  
Results of CEC

Sample	CEC (meq/kg)
Coarse/raw	149.6
Coarse/washed	167.2
Coarse/acid-treated	61.6
Medium/raw	158.4
Medium/washed	162.8
Medium/acid-treated	50.6

CEC values. As for acid-treated samples, there was a significant difference in CEC 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. Based on the above, one may mention that the treatment of material with acid probably leave some residual acid traces which then further "contaminate" the samples. These results were also consistent with the relevant porosimetry results and are similar with what is reported in other studies [20].

### 3.3. X-ray diffraction

Fig. 3 shows the X-ray diffraction spectrum of the natural palygorskite (raw). Here the characteristic peak at  $8.5^\circ$  (1.05 nm) is attributed to the existence of the palygorskite natural mineral. The characteristic peaks at  $14.0^\circ$  (0.62 nm) and  $28.1^\circ$  (0.32 nm) are also attributed to the natural palygorskite [21]. On the other hand, the characteristic peak at  $26.6^\circ$  (0.34 nm) is attributed to the presence of quartz. Similar spectrum is reported in the recent literature [21].

### 3.4. Total adsorption capacity

In the case of  $Cu^{2+}$  adsorption, the results obtained by the total adsorption determination revealed, as expected, the great dependency of the phenomenon with varying pH

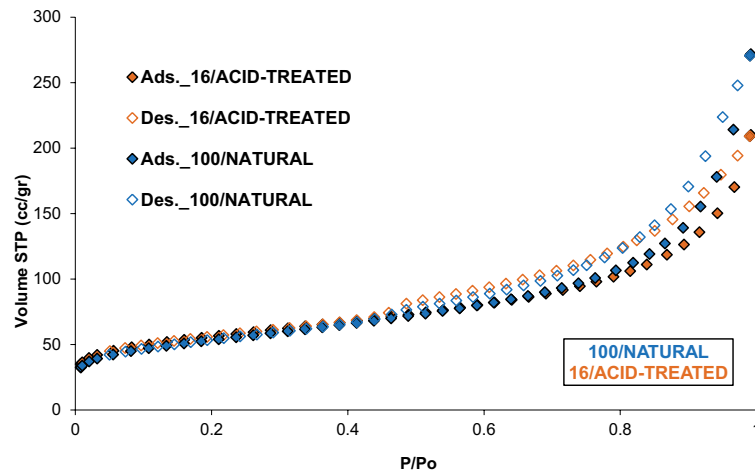


Fig. 2.  $N_2$  adsorption isotherm at 77 K for fine/raw and coarse/acid-treated.

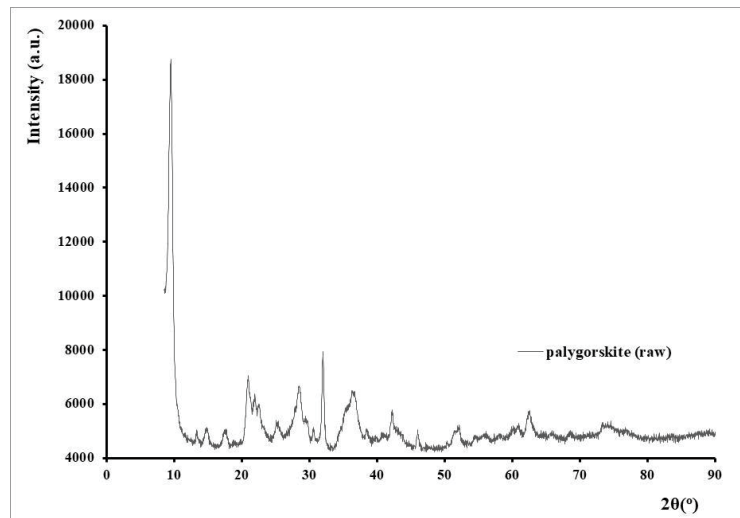


Fig. 3. X-ray diffraction pattern of natural palygorskite material.

and are presented in Table 1. Based on these data it is concluded that the more beneficial conditions were when the temperature was 15°C and the pH 8.5. The sample's particle size didn't play any important role. As the pH becomes acidic (pH = 3.0), the quantity of the total adsorption decreased significantly, especially in 15°C. The differences of the results between particle size and treatment of the palygorskite weren't noteworthy.

The palygorskite showed adsorption capacity up to 30 mg/g, comparable with the literature [22,23]. As it is obvious in Table 3 and Fig. 4 the pH of the solutions was the most important parameter, irrespective of temperature change, particle size distribution and material modification.

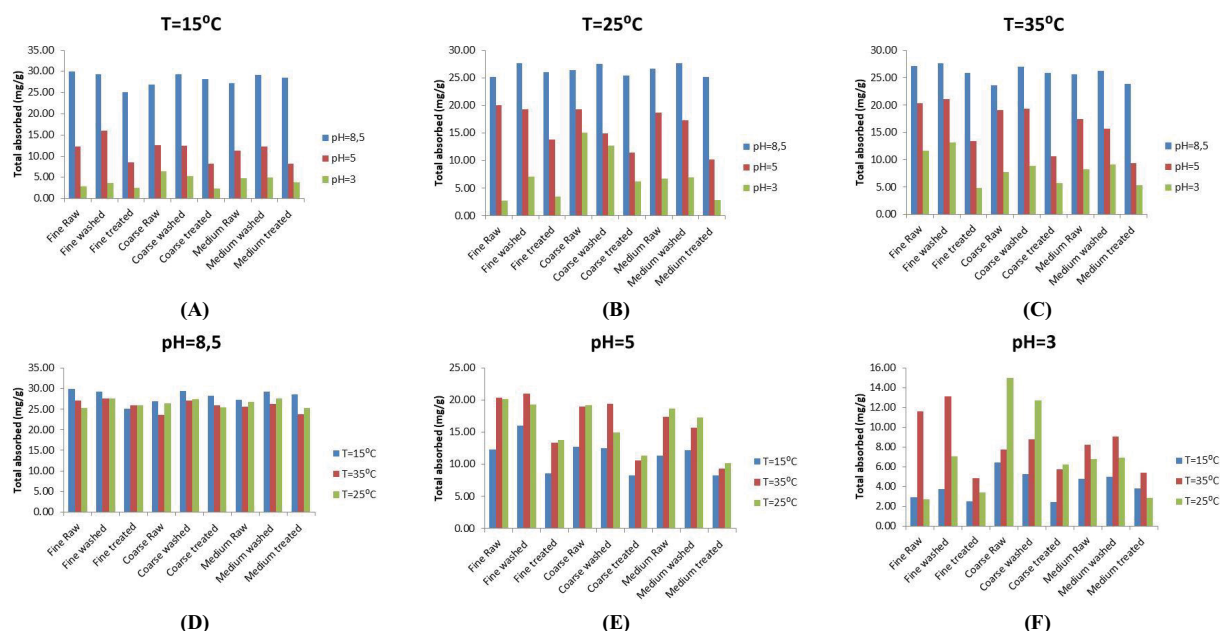
It is widely known that the adsorption process is a multi-parametric phenomenon in which the major factors are the solution's pH and temperature. Those factors can strongly affect the final adsorption capacity of the materials. Based on Table 3, it is clear that in the case of strong acidic conditions (pH 3.0), the increase of the temperature from 15°C to 25°C caused an increase of the adsorption

capacity ranging from 20% (coarse raw sample) to 294% (fine raw sample); the average increase was calculated to be 116%. Similar behavior was observed in the case of mild acidic conditions (pH 5.0); the increase of the temperature from 15°C to 25°C caused an increase of the adsorption capacity ranging from 13% (medium acid-treated sample) to 65% (fine raw sample) – the average increase was calculated to be 42%. However, a reverse behavior was observed in the case of alkaline conditions (pH 8.5) where by increasing the temperature from 15°C to 25°C, a very slight decrease of adsorption capacity was observed; the increase of the temperature from 15°C to 25°C caused a decrease of the adsorption capacity ranging from 6% (fine washed sample) to 17% (medium acid-treated sample) – the average increase was calculated to be 42%. The first point to mention is that the optimum conditions for the adsorption was found to be alkaline. This can be explained taking into consideration the nature of the ions (copper cations), so at these conditions the excess of hydroxyl groups ( $OH^-$ ) of the solution favors the interaction of the

Table 3

Total adsorption capacity of nine studied palygorskite samples at 15°C, 15°C and 35°C and at pH 3.0, 5.0 and 8.5

pH	Total adsorbed amount (mg/g)								
	pH = 8.5			pH = 5.0			pH = 3.0		
	Temperatures	T = 15°C	T = 25°C	T = 35°C	T = 15°C	T = 25°C	T = 35°C	T = 15°C	T = 25°C
Fine/raw	29.97	25.21	27.08	12.28	20.09	20.32	2.94	2.73	11.59
Fine/washed	29.29	27.60	27.57	15.96	19.33	21.02	3.74	7.04	13.10
Fine/acid-treated	25.16	25.97	25.91	8.58	13.77	13.38	2.50	3.43	4.85
Coarse/raw	26.88	26.37	23.62	12.67	19.23	19.02	6.44	14.99	7.73
Coarse/washed	29.42	27.48	27.04	12.53	14.97	19.35	5.27	12.67	8.78
Coarse/acid-treated	28.18	25.41	25.84	8.22	11.37	10.55	2.45	6.23	5.73
Medium/raw	27.24	26.70	25.64	11.36	18.63	17.43	4.79	6.75	8.22
Medium/washed	29.17	27.60	26.18	12.22	17.27	15.67	5.01	6.90	9.03
Medium/acid-treated	28.56	25.18	23.80	8.22	10.18	9.31	3.78	2.84	5.37

Fig. 4. (A–C) Total adsorption capacity in  $T = 15^{\circ}\text{C}$ ,  $25^{\circ}\text{C}$  and  $35^{\circ}\text{C}$  for  $\text{pH} = 3.0, 5.0, 8, 5$ , and (D–F) total adsorption capacity at  $\text{pH} = 8.5, 5.0$  and  $3.0$  for  $T = 15^{\circ}\text{C}, 25^{\circ}\text{C}$ , and  $35^{\circ}\text{C}$ , respectively.

samples with the cations. By increasing the temperature of the solution, the mobility of the cations in the solution becomes higher and therefore the capacity increases. On the other hand, at acidic conditions (strong or mild), the excess of the hydrocations ( $\text{H}^+$ ) does not favor the interaction of copper ions (cations) with the functional groups of the material. The increase of the temperature, increases not only the mobility of copper ions, but also of  $\text{H}^+$ , so the probable adsorption interactions become more difficult. The latter explanation is based on fundamentals of physico-chemistry and this is the reason that usually we check the effect of temperature only on optimum pH conditions (in which the adsorption is favored). To check the adsorption capacity of the materials used, a comparative table is given in following (Table 4).

In the case of dye adsorption, the results obtained by the total adsorption determination revealed, higher adsorption capacity than in the case of copper ions removal. The latter can be attribute to the more in number functional sites of Methylene blue molecule which can easily interact with the adsorbent material. Taking into account that the sample is the same both in dye and copper ions adsorption, the charge and functional groups are the same, so the difference can be only attributed to the different pollutant. Similarly, the most favorable conditions were in the alkaline region ( $\text{pH} = 8.5$ ) which is clearly due to the cationic nature of the dye molecule (it has located positive amino group). Also, the increase in temperature from  $15^{\circ}\text{C}$  ( $54.87 \text{ mg/g}$ ) to  $25^{\circ}\text{C}$  ( $72.32 \text{ mg/g}$ ) caused an improvement of 32% in the adsorption performance of

the material. Further increase to 35°C (125.44 mg/g) drastically increased the adsorption capacity by 129% (Fig. 5). The latter adsorption behavior is common, because the increase of temperature “helps” the movement of dye molecules in the solution and therefore their contact with the active adsorption sites becomes easier.

3.5. Fixed-bed column experiments

As is already indicated by batch experiments, the pH of feed solution is an important controlling factor in

Table 4  
Maximum adsorption capacities of various clay minerals for copper ions removal

Natural sorbent	$q_m$ (mg/g)	Reference
ZrO-montmorillonite	7.10	[24]
Na-bentonite	17.87	[25]
Na-montmorillonite	33.33	[26]
Bentonite polyacrylamide composite	11.36	[27]
Goethite modified bentonite	9.90	[28]
Humic acid modified bentonite	10.33	[28]
Montmorillonite-illite	30.99	[29]
Montmorillonite	17.88	[30]
Natural clay	44.84	[31]
Kaolinite	10.78	[32]
Goethite	37.25	[33]
Montmorillonite	13.27	[34]
Functionalised bentonite	45.80	[35]
Kaolinite	4.42	[36]
Palygorskite	2.35	[37]
Spent activated clay	10.90	[38]
Montmorillonite	7.61	[34]
Clinoptilolite	13.60	[39]
Siderite	19.80	[40]

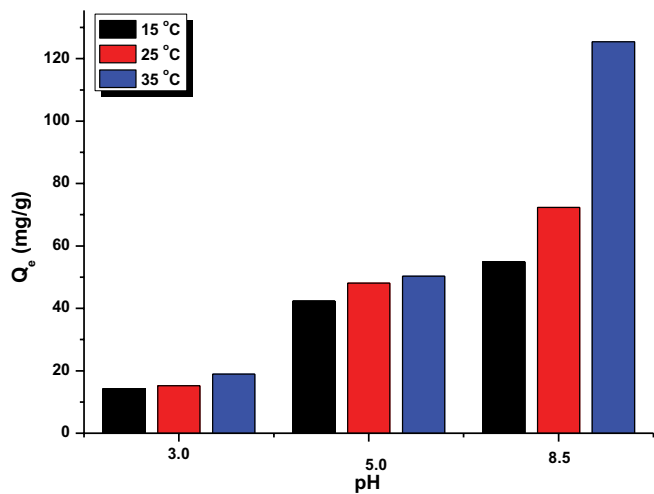


Fig. 5. Total adsorption capacity in  $T = 15^\circ\text{C}$ ,  $25^\circ\text{C}$  and  $35^\circ\text{C}$  for  $\text{pH} = 3.0, 5.0, 8.5$ , for the removal of Methylene blue by coarse raw.

the heavy metal adsorption process. Based on this fact solutions at different pH, namely 8.5, 5.0 and 3.0 were used to monitor the behaviour of the column. As the best results were obtained in the case of pH5 we present the breakthrough curves only of this pH experiments (Figs. 6 and 7).

Here must be also noted that among the three studied samples the sample “fine” is not able to be used in column experiments as the pressure became too high and the solution flow was blocked. This happened because of the very small particle size of the material. A small increase of the column pressure, during the exploitation of the experiments,

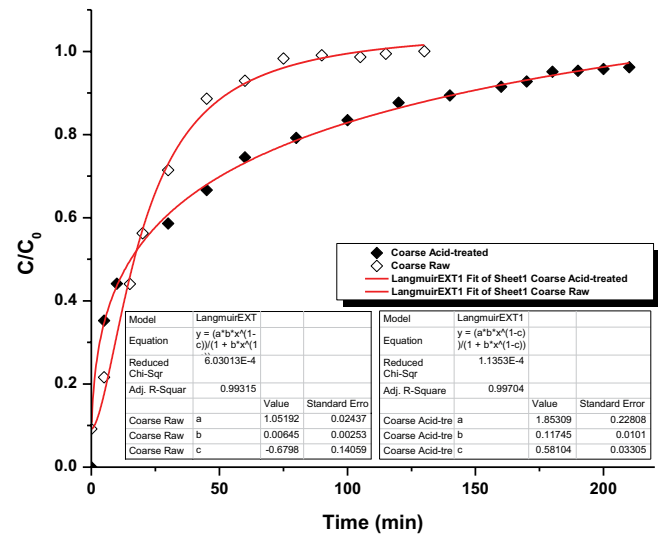


Fig. 6. Breakthrough curves at 4.8 mg/L inlet concentration at flow rate of 40 mL/min for samples “coarse raw” and “coarse acid-treated” ( $25^\circ\text{C}$ ,  $\text{pH} = 5.0$ ). The solid lines represent the fitting curves of the Langmuir EXT1 model.

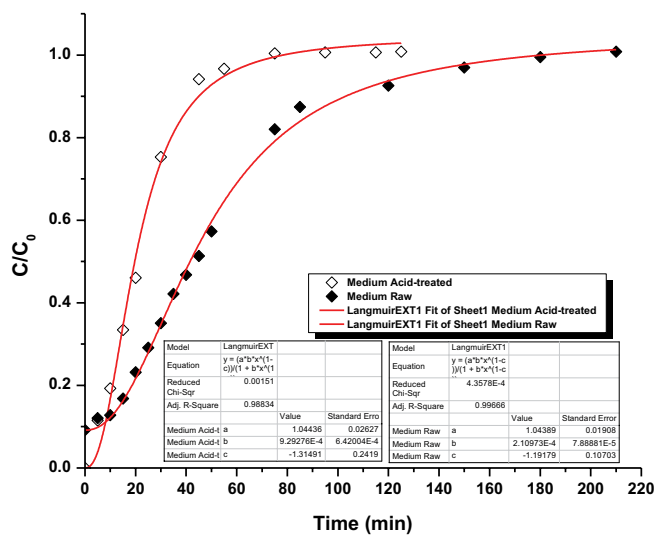


Fig. 7. Breakthrough curves at 4.8 mg/L inlet concentration at flow rate of 40 mL/min for samples “medium raw” and “medium acid-treated” ( $25^\circ\text{C}$ ,  $\text{pH} = 5.0$ ). The solid lines represent the fitting curves of the Langmuir EXT1 model.



Table 5  
Langmuir model equation fitting parameters for Cu<sup>2+</sup> adsorption isotherms at 25°C, pH = 5.0, for the four studied samples

Sample	Langmuir $q_m$ (mg/g)	$b$	$R^2$
Medium/raw	45.94	$2.1 \times 10^{-4}$	0.996
Medium/acid-treated	23.00	$9.3 \times 10^{-4}$	0.988
Coarse/raw	35.05	$6.45 \times 10^{-3}$	0.993
Coarse/acid-treated	20.83	$1.17 \times 10^{-3}$	0.997

was also observed in the case of the “medium acid-treated” sample.

As it is shown in Figs. 6 and 7 the breakthrough curves of the continuous flow experiments for all studied samples, follow the characteristic sigmoidal curve. For Cu<sup>2+</sup> adsorption on palygorskite under study, the highest maximum bed capacity and the longest breakthrough time is obtained at coarse raw sample.

Adsorptions with “medium” samples in the same parameters (raw, 25°C, pH = 5.0) were also presented stable pressure through the whole duration, approximately at 600 mbar without high pressure. The adsorption process through breakthrough experiment had a normal breakthrough curve that took place 210 min, with initial concentration of copper ions approximately at 5 mg/L. Langmuir EXT1 used to fit to experimental data for determination of the total adsorbed amount  $q_{total}$  for copper, calculated equal to 45.94 and 23 mg/g for “medium raw” and “medium acid-treated” respectively, according to equation (3).

The Langmuir EXT1 isotherm model was in excellent agreement with the experimental results as suggested by  $R^2$  also for “coarse” samples. In the case of medium samples (raw and acid-treated) the Langmuir maximum adsorption capacity was 35.05 mg and 20.83 mg/g, respectively (Table 5).

At both cases the total adsorbed amount decreased in the case of the acid-treated samples. This can be attributed to the fact that the treatment with the acid removed, on the surface, active places for copper ion adsorption.

#### 4. Conclusions

Cu<sup>2+</sup> adsorption was studied for different palygorskite samples in a pH range of 3 to 8.5. In summary, the basic parameter which affects the total adsorption capacity of Cu<sup>2+</sup> is the pH whereas the particle size, the temperature and the acid treatment of the material play insignificant role on the adsorption phenomenon. The basic environment was the favorable for the adsorption. In acidic environments, there was a decrease in the kinetics of the adsorption as well as in the total amount of adsorbed Cu<sup>2+</sup>. The higher adsorption capacity of Methylene blue dye was also observed at pH = 8.5. Further investigation on binary, heavy metal and dyes, systems will be performed.

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