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ADSORPTION PROPERTIES OF ROW AND CHEMICAL ACTIVATED GRAIN-MATERIAL DERIVED FROM NATURAL SAND OF ALBANIAN COASTLINE

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ABSTRACT

The present paper investigates the adsorption properties of a natural material obtained from the sand of Albanian coastline. The heaviest fraction of the natural material is processed through mechanical and chemical activation to obtain different forms of the grain materials. Mechanical activation under wet and dry conditions was applied using 1% and 10% H_2SO_4. Two consecutive mechanical stages followed by chemical activation were compared with simultaneous activation of the absorbent. The differently-prepared grain materials have been investigated in relation to their adsorption properties with Cu^{+2}. The experimental data were fitted into Langmuir and Freundlich isotherms theoretical model for the investigation of the adsorption procedure. Once the data were linearized, the adsorption parameters were calculated. The linearization of Freundlich equation provided the highest values of correlation coefficient, confirming that the adsorption of Cu occurs according to a heterogeneous and non-monolayer process. The differences found are related with the value of n calculated for the mechanical and chemically activated samples. Regarding the mechanical activated grain material, $n<1$ shows the probability of chemical adsorption; while the effect of chemical activation of the grain material, is expressed in the increase of the value of n which means gradual transition from chemical adsorption to physical ones.

Keywords: adsorption, isotherm, grain material

1. INTRODUCTION

Heavy metals constitute a very heterogeneous group of elements widely varied in their chemical properties and biological functions. In addition, they are kept under environmental pollutant category due to their toxic effects on living species. Consequently, constant attention has been paid to their removal, especially from aquatic environments. Some of the techniques for removing heavy metals from aquatic environments are based on the processes of precipitation, filtration, ion exchange, etc. Meanwhile, techniques based on adsorption processes are of particular interest, especially when relatively low cost adsorbents are used. Water purification from Ni, As, and Cu, Cd and Pb has been respectively investigated in (Janusz and Skwarek 2005; Mavropoulos *et al*., 2005; Mayo *et al*., 2007; Vaclavikova *et al*., 2010; Zhang *et al*., 2020) based on the adsorption properties of some natural materials classified in the group of ilmenite-magnetite materials. Their adsorbent properties are related to the presence of TiO2 and/or Fe_2O_3. Also coastal sands containing oxides of silicon, iron, etc. (Vasjari et al.,) can be used in rapid filtration processes to remove metals from water as a result of adsorption processes. The primary objective of the present paper is the application of innovative methods employing grain materials with adsorptive properties for environmental purposes. The preparation and use of these materials which utilize industrial waste for the development of environmental cleaning technologies is an example of the "circular economy". A circular economy (also referred to as circularity and CE) is a model of production and consumption, which involves sharing, leasing, reusing, repairing, refurbishing and recycling existing materials and products as long as possible. The material here investigated was obtained from the Old Sand Enrichment Plant, Durres, and its chemical composition (Vasjari et al.,) makes it a likely adsorbent for metals. The natural material has been pre-treated through mechanical activation under various experimental conditions for better adsorptive properties to heavy metals. Investigation on copper ion affinity involving theoretical adsorption isotherms and linearization of the data was a means to address the present experiment.

2. MATERIALS AND METHODS

In the present investigation, reagents of analytical grade were used to prepare the required aqueous solutions. Adsorption isotherms employing different concentrations of Cu^{2+} aqueous solution, at room temperature, were used for the investigation of the adsorption process. There are two modes of absorbent preparation: i) dry mechanical activation followed by chemical

activation (treatment in aqueous solution with different pH) and, ii) simultaneous mechanical and chemical activation.

In the first case, once grinded, the material was analyzed for its particle size distribution through a sieve system by dividing it into 6 fractions with the following size ranges: i) 0.50-0.25 mm, ii) 0.25- 0.125mm, c) 0.125-0.10mm, iii) 0.10-0.09mm, iv) 90-71µm and, v) 71-56 µm. Based on preliminary studies performed in the laboratory (Broli 2013) the 90-71 µm fraction was selected which underwent the acidic activation process.

The chemical activation was performed in plastic tube of 50 ml. 5 g from the selected fraction (71-90µm) were weighed and 1% or 10% H_2SO_4 solution was added. The prepared suspension was placed in a shaker for 12 hours. Once decanted, it was filtered, rinsed with distilled water several times and placed in a thermostat at 60ºC overnight.

In the second case, the agate sphere mill, a device that ensures fine grinding of the materials in wet condition using different pH solution was used for the preparation procedure (Hanke 2014; Phoohinkong *et al*., 2017). The inner part of the equipment which is in contact with the material and working solutions is a by-inert material avoiding the reaction with the materials to be treated in it. The spheres are also made of agate, a strong and inert material also.

A certain amount of natural material (table 1) was placed in the milling container together with the solution which will realize the chemical activation of the material during grinding. 1% H_2SO_4 solution and 10% H_2SO_4 solution for 4 hours were used for chemical activation purposes. Once decanted, the crushed solid material was filtered, rinsed with distilled water several times and placed in a thermostat at 60ºC overnight. The prepared grain materials were fractionated using the sieve system, and each fraction was weighed to estimate losses (tab 1).

Table 1 Distribution of material by fractions (in gr.)

	Preparation procedure	**Initial weight (g)**	>100 µm	100-90 µm	90-71 µm	71-63 µm	$\sum fractions$ (g)
2	Chemical activation 1% H_2SO_4	12.45	4.82	0.34	0.54	6.45	12.15
3	Chemical activation 10% H_2SO_4	11.53	3.53	0.33	0.63	6.86	11.35

Adsorption experiment: An amount of activated material was placed in contact with 15 ml of a standard solution of Cu^{+2} (5 to 200 ppm). The systems

were kept for 12 hours at room temperature under continuous mixing conditions using Roll MIXER (80 rrot / min). The Hettich EBA 20 centrifuge for 5 min at 45,000 rpm was used to separate solution from the solid phase (adsorbent). The Flame Atomic Absorption Spectroscopy (Specter AA-10 plus) was involved for the concentration of Cu^{+2} in the solutions before and after the adsorption process. The amount of adsorbed Cu is calculated and expressed in mgCu /gr absorbent.

Langmuir Isotherm model and Freundlich's model are used to evaluate the adsorption parameters. This isotherm model is based on the assumptions that the adsorption process occurs at particular homogeneous sites on the surface of the adsorbent. In addition, it allows to calculate the maximum adsorption in monolayer through the parameter X_{max} expressed in mg analyte per gram adsorbent. The Freundlich isotherm model predicts a heterogeneous adsorption process and provides the opportunity to judge whether adsorption is characterized by chemical or physical interactions through the value of the parameter n. Both models provide information on the affinity of analyte adsorption to the adsorbent through the constant K.

The table 2 summarizes the experimental results of the Cu+2 absorption from the mechanical activated material. The amount of absorbed Cu is calculated and expressed in mgCu/gr absorbent is in this table reported. Logarithmic values necessary for of the data linearization are also reported. Figure 1 depicts the absorption curve, while the linearization of the data according to Langmuir and Freundlich's theoretical model are in the Figure 2 and 3 respectively depicted.

The same procedure is followed in all experiments using activated material in different modes. Figure 4(a) and (b) depict the results of data linearization when the activated material in H_2SO_4 1% used applying the first procedure (mechanical and chemical activation simultaneously). Figure 4(c) and (d) represent the case of activated material via dry mechanical activation and wet chemical activation in H_2SO_4 10%.

Table 2 Adsorption data of Cu from mechanical activated grain material

Nr	Adsorbent (g)	Initial concentration C (ppm)	Final concentration C (ppm)	ΔC (ppm)	Adsorbed (mg Cu /g)	log(C_{ads})	logC
1	0.0202	5	4.75	0.25	0.12	-0.90	0.70
2	0.0217	10	9.88	0.12	0.06	-1.25	1.00
3	0.02	15	14.52	0.48	0.24	-0.62	1.18
4	0.0208	25	23.12	1.88	0.90	-0.04	1.40
5	0.0213	50	44.47	5.53	2.59	0.41	1.70
6	0.0228	100	90.31	9.69	4.25	0.63	2.00
7	0.0242	150	131.99	18.01	7.44	0.87	2.18
8	0.0212	200	177.90	22.10	10.42	1.02	2.30

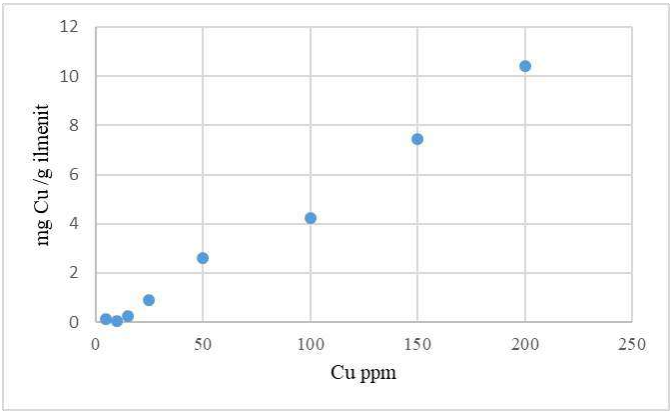

Fig 1: Adsorption isotherm using mechanical activated grain material.

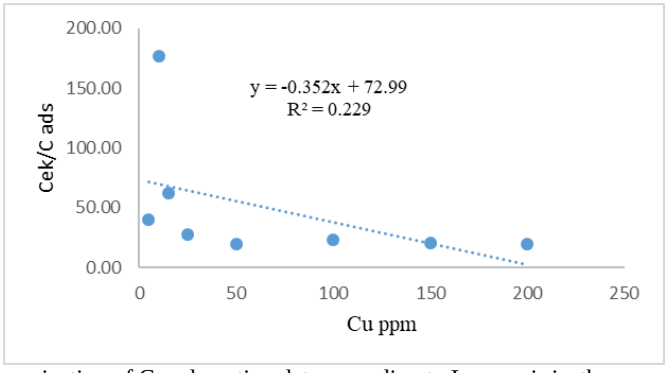

Fig. 2: Linearization of Cu adsorption data according to Langmuir isotherm model using mechanical activated grain material.

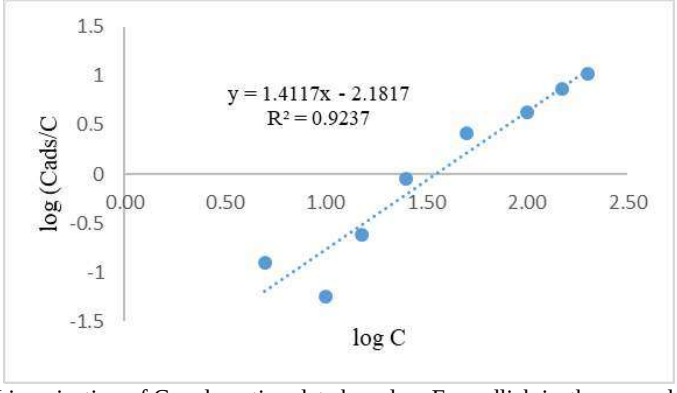

Fig 3: Linearization of Cu adsorption data based on Freundlich isotherm model using mechanical activated grain material.

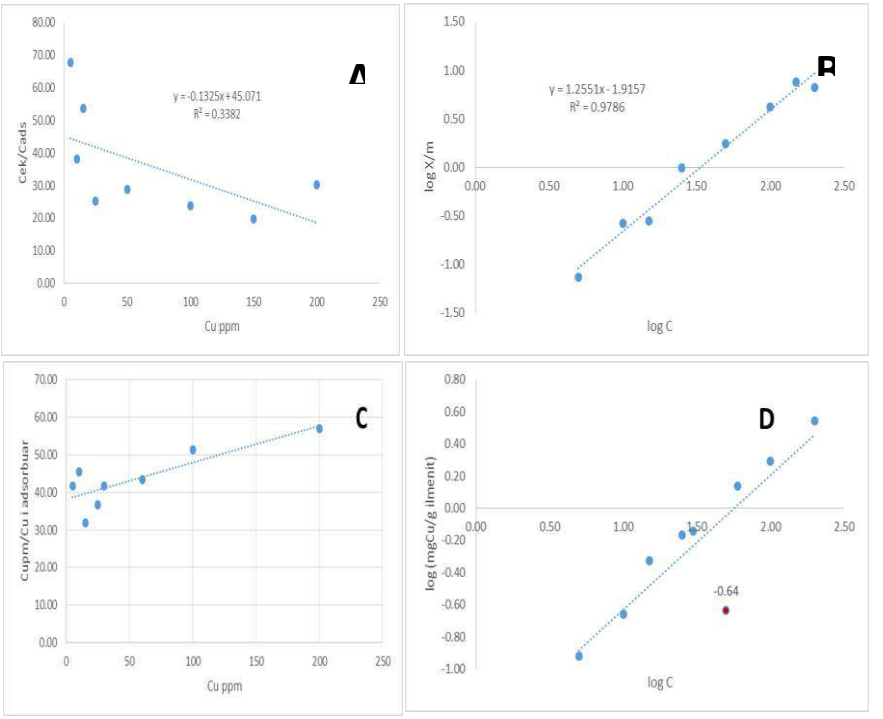

Fig. 4: Linearization of absorption isotherms: a) activated material in H_2SO_4 1% -Langmuir model; b) activated material in H_2SO_4 1% -Freundlich model; c) activated material in H_2SO_4 10%- Langmuir model; d) activated material in H_2SO_4 10%- Freundlich model.

3. DISCUSSIONS

Langmuir isotherm, in its general form is given as the degree of coverage of the surface (active centers), depending on the concentration of the solution in contact with it, in equilibrium conditions:

a. $$x_{ek} = \frac{X_{\max} K C_{ek}}{1 + K C_{ek}}$$

where X-ek is the amount of Cu^{+2} adsorbed (g Cu / g adsorbent) corresponding to C-ek of the analyte in the solution. X-max is the adsorption capacity of the material, or the maximum amount of Cu^{+2} adsorbed from 1g adsorbent. K is a constant for a given system which represents the affinity of Cu^{+2} for the adsorbent. Referring to the certain adsorbent system, the smaller the value of K, the greater the affinity between analyte to adsorbent. To find the constant K as well as the maximum amount that can be adsorbed by 1 g of adsorbent, the isotherm equation can be linearized as follows:

$$\frac{C_{ek}}{X_{ek}} = \frac{1}{X_{\max} K} + \frac{C_{ek}}{X_{\max}}$$

The linearization of the data following to the Langmuir theoretical model for only mechanical activated grain material (fig.2), as well as for mechanical and chemical activated grain material are given in table 3. In the case of mechanical activated grain material the negative value of the slope of the curve from which C_{max} should be calculated as well as worst correlation coefficient, indicates that the adsorption of this grain material cannot be explained by this model. For chemical activated material in H_2SO_4 1% or 10% linearization of experimental data according to the Langmuir theoretical model results in a correlation coefficient of 0.3382 and 0.6861, respectively (Fig. 4 (a) and (c)). This means that adsorption does not approach the assumptions of this theory for monolayer and homogeneous adsorption.

Table 3 Summary of adsorption results

Preparation procedure	**Theoretical model**	**Linearization of the data**	**R^2**	**Adsorption parameters**	
				K	**X_{max}** (mg/g)/n
2 steps: * Dry mechanical activation * Wet chemical activation (H_2SO_4 10%)	Langmuir	Y = 0.098 x + 38	0.6861	$2*10^{-3}$	10.2
	Freindlich	Y =0.906 x – 1.49	0.9844	$10^{-1.5}$	1.10
1 step *Wet mechanical and chemical activation simultaneously (H_2SO_4 1%)	Langmuir	Y =-0.132 x + 45.07	0.3382	-	-
	Freindlich	Y = 1.2551 x – 1.92	0.9786	$10^{-1.9}$	0.80
Dry mechanical activation	Langmuir	Y =-0.352 x + 72.99	0.2290	-	-
	Freindlich	Y = 1.4117 x – 2.18	0.9237	$10^{-2.2}$	0.71

To prove that adsorption can occur according to a multi-layered and heterogeneous model, the experimental data obtained are fitted to Freundlich's theoretical model. According to the Freundlich model, the relationship between adsorption and analyte concentration in solution is given by the equation:

$$\frac{C_{ads}}{C} = K * C^{\frac{1}{n}}$$

where K and n are two characteristic adsorption constants. K provides information on the adsorption capacity, the affinity between the analyte and the adsorbent. The n indicates the intensity of adsorption. The value of n indicates the deviation from the linearity of the adsorption dependence of the analyte concentration in the solution: i.e. if it results in n = 1, then the adsorption is linear; if n <1 adsorption is a chemical process; while in n> 1 the adsorption process is physical (Desta 2013).

The linearization of this equation is given as a dependence:

$$log\frac{C_{ads}}{C} = logK + \frac{1}{n}logC$$

The linearization of the experimental data obtained for mechanical activated grain material according to the Freindlich theoretical is shown in Fig 3. The value of the correlation coefficient is acceptable for the linear dependence R^2 = 0.9237. From the parameters of the straight line the affinity is evaluated presented by calculated K = $10^{-2.18}$ while the value of n = 0.71 suggest the chemical adsorption (n <1).

Regarding the grain materials activated in H_2SO_4 1% or 10%, linearization of experimental data has resulted in a very good correlation with R^2 = 0.9786 and R^2 = 0.9844, respectively, as based on Friendlicht's theoretical model. The values of the n coefficient increase as pH (increasing the concentration of H_2SO_4 during activation) decreases, which means that the intensity of adsorption increases. Based on the results obtained, independently by the preparation procedure of the grain material, the data show the very good fitting to the Freundlich's theoretical model. Surface characterization using SEM and EDS analyzes of the chemically activated samples (Vasjari et al.,), has shown that the particles of the grain material of absorbent have irregular shape, high surface roughness and the chemical composition of the surface varies depending on the chemical activation. This explains the Cu absorption due to heterogeneous and multilayers form.

4. CONCLUSIONS

The absorption of Cu from the experimented material, derived from the sand and prepared differently using mechanical activation and/or chemical activation is studied based on Langmuir and Freundlich theoretical models of adsorption. The experimental data fit very well to theoretical model of Freundlich. Consequently, Cu^{2+} adsorption is a heterogeneous process on a heterogeneous surface.

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