

Batch Sorption of Zn^{2+} and Cd^{2+} from Wastewater using “Kosovo” Clay as a Low Cost Adsorbent

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Abstract– Kosovo clay in its natural and treated form, obtained from Kamenica, state Kosovo was utilized as a low-cost adsorbent for Zn^{2+} and Cd^{2+} ions from solution. Experiments were carried out as a function of initial concentration of ions and contact time with clay while the amount of adsorbent was kept unchanged. From the results obtained, it was found that the removal of ions depends on concentration and contact time. In treatment with clay, the removal of metal ions from sample is high whereby the percentage of removal is more than 90 percent of the initial concentration. The efficiency of the untreated clay for the removal of heavy metal ions from solution is greater than that of clay treated with sulfuric acid. The adsorption isotherms could be fitted well by the Langmuir model. The *RL* value in the present investigation was less than one, indicating that the adsorption of the metal ion onto this clay is favorable.

Keywords– Natural Clay, Treated Clay, Adsorbtion, Zn^{2+} , Cd^{2+} , Equilibrium and Isotherm

I. INTRODUCTION

The pollution by heavy metals currently it is becoming a big challenge and a concern for the water quality and also for the environment in general [1]. Some metal ions are toxic even if their concentration is very low, and their toxicity increases with accumulation in water and soils [2].

Traditional technologies for the removal of heavy metals from water and waste water include precipitation, ion exchange, adsorbtion, coagulation, electrolysis, extraction membrane separation and reverse osmosis [3]-[5].

Adsorbtion is now recognized as an effective and economic method for heavy metal waste water treatment. The adsorbtion process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. Various substances, such as activated carbon, natural and synthetic zeolites, aluminosilicate (clay minerals) and ion exchange resins have been used as adsorbents for the removal of heavy metals from water and wastewater [6].

Clay has typical properties (larg surface area, high cation exchange capacity chemical and mechanical stability and a layered structure) that predispose them to be good adsorbents. Bentonite belongs to the group of clay minerals. A number of studies have shown their effectiveness for the removal of metal ions [7].

However, the sorbing properties of clays for heavy metal ions must be characterized in order to predict the behavior and

removal of toxic heavy metals from industrial wastewaters is still remains a technological challenge [8]-[12].

Clay features are strongly dependent on the activation procedure. Acid treatment is expected to improve the specific surface area and porosity, unless the clay framework collapses, more particularly under severe activation conditions. Chemical changes after acid treatment for bentonite induce surface morphology modifications, resulting in significant differences in the substrate affinity for heavy metal ion, before and after treatment [13].

Adsorption isotherm is an empirical relationship used to predict how much solute can be adsorbed by activated carbon [14]. Adsorption isotherm is defined as a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent (e.g., activated carbon) and the amount of adsorbate remaining in a test medium at equilibrium, and it shows the distribution of adsorbable solute between the liquid and solid phases at various equilibrium concentrations [15]. The three wellknown isotherms are: a) Freundlich, b) Langmuir, and c) BET adsorption isotherm [14].

Then, the main objective of this paper was to investigate the data on the efficiency of native and acid activated bentonite in removing Cd^{2+} and Zn^{2+} ions from aqueous systems.

II. MATERIAL AND METHODS

A) Reagents and solutions

All the reagents used were of analytical grade and distilled de-ionized water was used in preparation of all solutions.

Solution of heavy metals, with different concentration was prepared by dissolving required quantity of their salts in the distilled demineralised water. The salts used are cadmium chloride and zinc chloride. Freshly prepared solution was used for each experiment.

B) Preparation of acid-activated bentonite

Kamenica’s (Kosovo) clay was obtained from Kamenica, Kosovo. The clay was dried and calcinated at 800 °C. After that the clay was treated with 1M sulphuric acid in water bath in relation 1g bentonite with 5ml acid. The composition was shaken for 1h. The acid treated clay was

centrifuged, air dried and ground to fine powder (< 0.12 mesh.)

C) Adsorption experiments

Adsorption tests were performed by batch experiments, under stirring at room temperature (20°C).

Each adsorption study was performed by adding 1g of the adsorbent to 5 ml of a given concentration of the adsorbate. At the end of the given contact time, the solid and liquid phases were separated by centrifugation. The amount of Zn²⁺ and Cd²⁺ ions remaining in the solution was determined using the AAS-- Parkin Elmer 370A flame atomic absorption spectrometer. All measurements were carried out in air/acetylene flame.

Each experiment was repeated and the mean value was calculated in order to minimize errors. The uptake capacity of the clay for Zn²⁺ and Cd²⁺ ions was calculated from the mass balance equation given in Eq. (1).

$$q_e = V[Co - Ce] / m \tag{1}$$

The percentage of Zn²⁺ and Cd²⁺ ions adsorbed was calculated from eq. (2).

$$\% \text{ Adsorb.} = [Co - Ce] / Co \times 100 \tag{2}$$

Where *q_e* is the uptake capacity (mg/g), *C_o* is the initial lead ion concentration (mg/l), *C_e* is the concentration of lead ion remaining in solution at equilibrium (mg/l), *V* is the volume of Zn²⁺ and Cd²⁺ ions solution used (liters) and *m* is the mass.

III. RESULTS AND DISCUSSION

A) Characterization of clay

The chemical composition of Kamenica's (Kosovo) clay obtained by classical method is shown in Table 1. It is observed that silica and alumina are the major constituents.

Table 1: Clay Composition

Composition	% by weight
SiO ₂	45.75
Al ₂ O ₃	13.61
K ₂ O	8.01
MgO	7.70
Fe ₂ O ₃	10.76
CaO	4.84
Na ₂ O	4.43

B) Effect of initial metal ion concentration

The initial metal ion concentration is an important factor to be considered in adsorption studies, since the rate of adsorption of an adsorbent for a metal ion is dependent on the initial concentration of metal ion present in solution. The effect of initial of Zn²⁺ and Cd²⁺ ions concentration on

adsorption by Kamenica (Kosovo) clay in its natural and treated form is presented in Fig. 1, Fig. 2, Fig. 3 and Fig. 4. respectively.

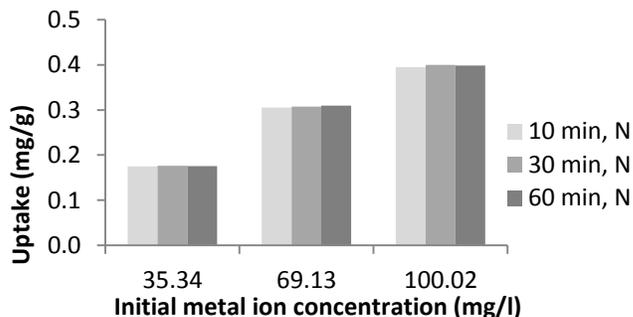


Fig. 1. Effect of initial Zn²⁺ concentration on the adsorption (natural clay)

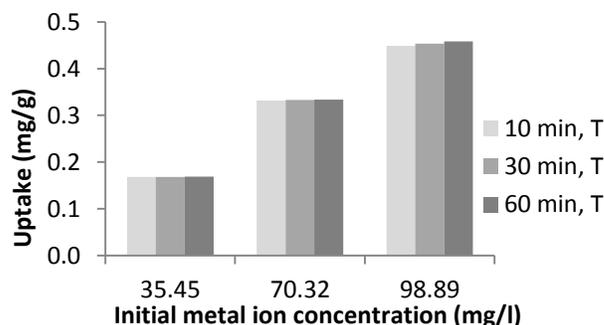


Fig. 2. Effect of initial Cd²⁺ concentration on the adsorption (natural clay)

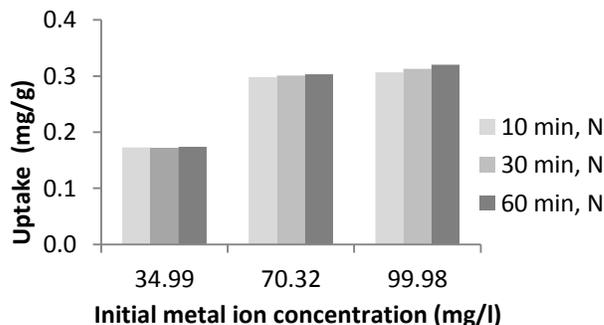


Fig. 3. Effect of initial Zn²⁺ concentration on the adsorption (treated clay)

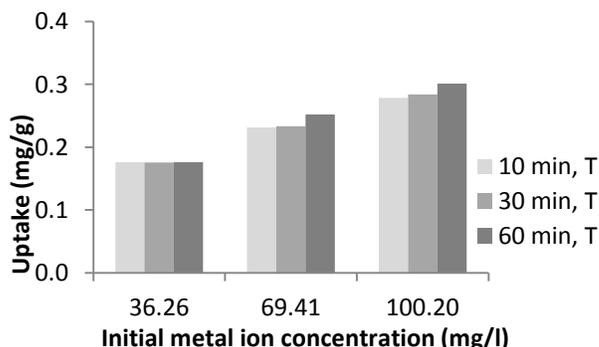


Fig. 4. Effect of initial Cd²⁺ concentration on the adsorption (treated clay)

It is seen that the uptake capacity of the clay for this metal ion increased with increase in initial concentration of ions. This increase is simply due to the presence of more metal ions in solution available for sorption. This increase in concentration increased the driving force overcoming resistances to mass transfer between the adsorbent and adsorbate species which led to the increase in adsorption observed [16].

C) Effect of time on adsorption

The effect of varying the sorption time is presented in Fig. 5 and Fig. 6 respectively.

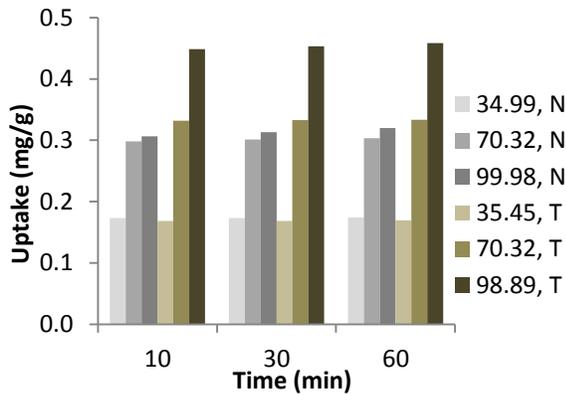


Fig. 5. Effect of contact time on the adsorption of Zn²⁺ on natural (N) and treated (T) clay

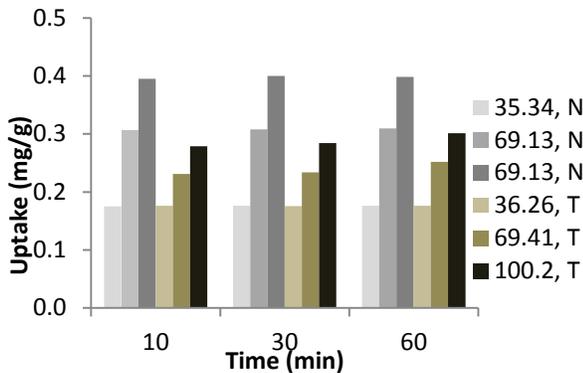


Fig. 6. Effect of contact time on the adsorption of Cd²⁺ on natural (N) and treated (T) clay

The adsorption rate was seen to increase rapidly at the initial stage, however, the equilibrium (maximum adsorption) was obtained in 60 minutes. The fast initial uptake is due to the availability of abundant active sites for sorption which became saturated with time [17].

D) Equilibrium Isotherms

The Langmuir and Freundlich adsorption isotherms were applied to the data obtained on the effect of initial metal ion concentration. Each isotherm was assessed based on the closeness of the value of the regression coefficient (R²) to one. The closer the R² value to 1 the more appropriate the isotherm [17].

Table 2: Equilibrium Parameters

Metal ion	Langmuir Isotherm			
	qm	b	R ²	R _L
Cd N	0.31	0.5	0.9876	0.0196
Cd T	0.41	0.94	0.9902	0.0105
Zn N	0.32	2.77	0.9998	0.0036
Zn T	0.87	0.16	0.976	0.0594
Metal ion	Freundlich Isotherm			
	n	Kf	R ²	
Cd N	6.13	0.24	0.9893	
Cd T	7.08	0.17	0.9819	
Zn N	8.12	0.22	0.9729	
Zn T	1.5	0.13	0.9743	

E) Langmuir Isotherm

This isotherm assumes that metal uptake occurs on a homogenous surface by monolayer adsorption without interactions between the active sites on the adsorbent or adsorbed metal ions [17]. The linearized form of the Langmuir isotherm is given in Eq. (3).

$$C_e/q_e = C_e/q_m + 1/q_m b \tag{3}$$

Where C_e (mg/l) is the concentration of heavy metal ions in equilibrium, q_e (mg/g) is the equilibrium uptake capacity, q_m (mg/g) is the maximum adsorption capacity corresponding to a complete monolayer coverage and b (l/mg) is the Langmuir isotherm constant which quantitatively reflects the affinity between the adsorbent and the adsorbate. A linear plot of C_e/q_e against C_e confirms the isotherm and is shown in Fig. 7 and Fig. 8.

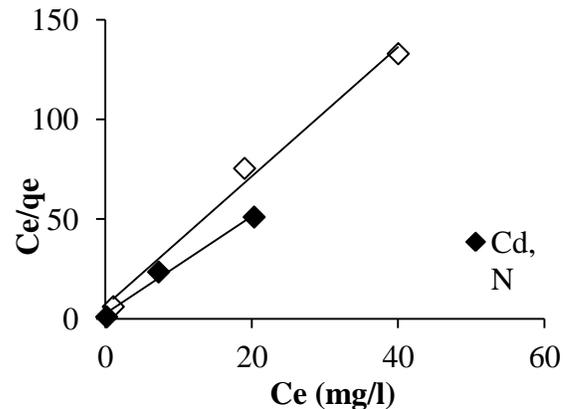


Fig. 7. Langmuir isotherm for adsorption of Zn²⁺ ions on natural (Zn,N) and treated (Zn, T) clay

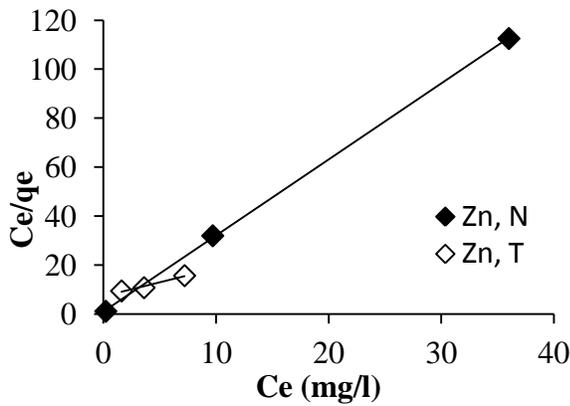


Fig. 8. Langmuir isotherm for adsorption of Cd²⁺ ions on natural (Cd,N) and treated (Cd, T) clay

The constants q_m and b were calculated from the slope and intercept respectively. The Langmuir isotherm parameters are given in Table 2. A low value of b indicates a favourable adsorption process. The value of b obtained is low which implies that the sorption of Zn²⁺ and Cd²⁺ ions onto our clay is a favorable one. The essential features of Langmuir adsorption isotherm parameter can be used to predict the affinity between the sorbate and sorbent using a dimensionless constant called separation factor or equilibrium parameter (R_L), which is expressed by the following relationship [19].

$$R_L = 1/(1+bC_0) \tag{4}$$

Where C_0 is initial metal ion concentration. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), linear ($R_L = 1$), unfavorable ($R_L > 1$), or favorable ($0 < R_L < 1$). The R_L values between 0 and 1 indicate favorable adsorption [19]. The R_L value in the present investigation was found to be 0.0036 - 0.0594 indicating that the adsorption of the metal ion onto our clay is favorable.

Langmuir and Freundlich adsorption constants and correlation coefficients (R^2) are presented in Table 2. The value of the regression coefficient (R^2) of this model is closer to 1 than that obtained for the Freundlich isotherm. This shows Langmuir adsorption isotherm was the better model for the metal ions adsorption onto clay with R^2 of 0.9998.

F). Freundlich Isotherm

The Freundlich isotherm unlike the Langmuir isotherm assumes that adsorption takes place on a heterogeneous surface which involves a multilayer adsorption of metal ions [18]. The linear form of the Freundlich equation is given in Eq. (4).

$$\ln q_e = \ln K_f + [1/n] \ln C_e \tag{4}$$

Where n is a dimensionless constant describing the adsorption intensity and K_f (L/g) is the Freundlich isotherm constant describing the adsorption capacity of the adsorbent. This isotherm was confirmed by the plot of $\ln q_e$ against $\ln C_e$

shown in Fig. 9 and Fig. 10. The constants n and K_f were obtained from the slope and intercept respectively. The Freundlich isotherm parameters are presented in Table 2. A value of n above unity indicates a favourable adsorption [18]. Again a favourable adsorption was obtained between Zn²⁺ and Cd²⁺ ions and our clay.

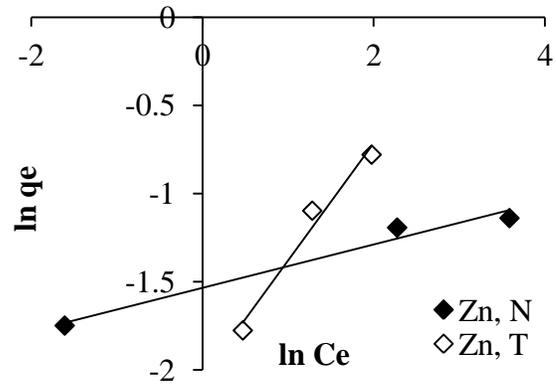


Fig. 9. Freundlich isotherm for adsorption of Zn²⁺ ions on natural (Zn,N) and treated (Zn, T) clay

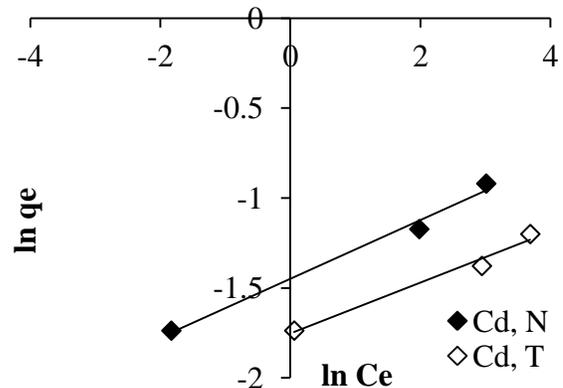


Fig. 10. Freundlich isotherm for adsorption of Zn²⁺ ions on natural (Cd,N) and treated (Cd, T) clay

The n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process. The n value in Freundlich equation was found to be 1.5–8.12, (Table 2). The situation $n > 1$ is most common and may be due to a distribution of surface sites or any factor that causes a decrease in adsorbent adsorbate interaction with increasing surface density and the values of n within the range of 1–10 represent good adsorption [19]. Increasingly large K_f value indicates greater adsorption capacity. $1/n$ is a function of the strength of the used adsorbent material. Value of $1/n$ high, showed adsorption bond is weak. When $1/n > 1$, the absorption coefficient increases with increasing concentration of the solution led to an increase in hydrophobic surface characteristics after monolayer. When the value of $1/n < 0$, K_f decreases with concentration [20]. In the present study, since

n lies between 1 and 10 it indicates the physical adsorption of metal ions onto clay.

IV. CONCLUSION

The batch adsorption of Zn^{2+} and Cd^{2+} ions onto Kamenica's (Kosovo) clay showed that the clay can be used as adsorbent for removal of these ions. Since clay is freely abundant, locally available, low-cost adsorbent and has a considerable high adsorption capacity, it may be treated as economically viable for removal of metal ions from water. Adsorption parameters such as initial metal ion concentration and contact time were useful in the description of the adsorption process. In both cases, linear plots were obtained, which reveal the applicability of these isotherms on the ongoing adsorption process.

The R_L value in the present investigation was less than one, indicating that the adsorption of the metal ions onto our clay is favorable. In treatment with clay, the removal of metal ions from sample is high whereby the percentage of removal is more than 90 percent of the initial concentration.

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