



## Adsorption of Cu<sup>2+</sup> and Mn<sup>2+</sup> From Aqueous Solutions by Kosovo Clay

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### ABSTRACT

In this work, batch adsorption experiments were carried out for the removal of copper and manganese ions as pollutant from aqueous solutions using Kosovo clay as the low-cost adsorbent in its natural and treated form. Results revealed that adsorption rate initially increased rapidly, and the optimal removal efficiency was reached within 60 min. The adsorption process obeys both Langmuir and Freundlich adsorption isotherms. The equilibrium parameter  $R_L$  in Langmuir isotherm, the Langmuir constants and Freundlich adsorption constants indicated that the adsorption of Cu<sup>2+</sup> and Mn<sup>2+</sup> on our clay was favorable. The batch adsorption of Cu<sup>2+</sup> and Mn<sup>2+</sup> ions on Kosovo clay showed that the clay can be used as a cheap alternative adsorbent for removal of these ions from aqueous solutions.

**Keywords:** Adsorption, copper ions, manganese ions, clay, isotherms.

### INTRODUCTION

Efforts to minimize production of hazardous waste and to remediate existing, accumulated waste have become one of the most important environmental challenges that the world faces today. According to recent surveys, the most common contaminants reported in groundwater are heavy metals. Therefore, inexpensive materials for removing and entrapping heavy metal wastes from contaminated water are required<sup>1</sup>.

Heavy metal ions in the aqueous environment such as Cu(II), Pb(II), Hg(II), Zn(II), As(V) and Cr(VI) mainly originate from industrial effluent<sup>2,3</sup>. These metal ions in water cause many toxic effects on the environment and human health<sup>4</sup>. The nonbiodegradability and long half-life of heavy metal ions leads to an accumulation of metal ions in the body of living creatures, causing diverse diseases such as poisoning, nervous system damage and cancer<sup>5</sup>. Therefore, it is essential to purify wastewater by removing its heavy metal content using efficient methods<sup>6</sup>.

Aqueous solutions containing copper ions have applications in the fields of mechanical manufacturing industry, electroplating, light industry and architecture. However, these solutions may cause serious lesions in the central nervous system and even permanent damage especially for children<sup>7</sup>.

Heavy metals like copper and manganese are the essential trace elements but show toxicity if in excess amounts in drinking water. Toxicity can result from any of the heavy metals if they are present less from its original limits in drinking water<sup>8</sup>.

According to EPA regulations, primary and secondary Maximum Contaminant Levels (MCL) of Cu in drinking water are respectively 1.3 mg/l and 1.0 mg/l whereas for Mn are respectively 0.0 and 0.05 mg/l.

In large doses, copper is dangerous to infants and people with certain metabolic disorders. However, lack of copper intake causes anemia, growth inhibition, and problems with blood circulation. In large doses, manganese can cause headaches, apathy, irritability, insomnia, and weakness of the legs. Long term heavy exposure may result in nervous system disorders.

Experimental studies on fetal development, investigating the toxic effect of manganese, showed that exposure to manganese results in a decrease in fetal weight and retardation of the development of the skeleton and internal organs<sup>9</sup>. In addition, manganese caused DNA damage and chromosomal aberrations and was toxic to the embryo and fetus<sup>10</sup>. Epidemiological studies of residents exposed to manganese revealed a neurotoxic effect<sup>11</sup> and Parkinson-like syndrome<sup>12</sup>. In individuals exposed to high levels of this metal, manganese can accumulate in various brain regions, leading to neurotoxicity<sup>13</sup>. It has been postulated that manganese may be involved in the generation of reactive oxygen species and production of oxidative stress<sup>14,15</sup>.

There are many technologies available for heavy metals removal. Among the available removal methods, adsorption, which is an efficient, economical and simple process, is widely used for low concentrations heavy metals.



Adsorption from the fields mentioned above or remediation of the contaminated environment using clay is practical, low in cost, efficient and environment-friendly approach.

The main objective of the present work was to investigate the performance of natural clay acid treated clay for the heavy metals ions remove from aqueous solution.

## MATERIALS AND METHODS

### 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 ( $\text{CuCl}_2$  and  $\text{MnCl}_2$ ) in water. Freshly prepared solution was used for each experiment.

### Preparation of Acid-Activated Bentonite

Kamenica's (Kosovo) clay was obtained from Kamenica, Kosovo. The clay was dried and 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.)

### 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 initial ( $C_0$ ) and equilibrium ( $C_e$ ) concentrations of  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  in the solutions were determined by flame atomic absorption spectrometer (Parkin Elmer 370A). 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 amount of  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  adsorbed was calculated from:

$$q_e = \frac{V \cdot (C_0 - C_e)}{m} \quad (1)$$

Percent removal of  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  ions was calculated according to equation 2.

$$R_{\%} = \left[ \frac{C_0 - C_e}{C_0} \right] * 100 \quad (2)$$

Where  $q_e$  is the uptake capacity (mg / g),  $C_0$  is the initial ion concentration (mg /  $\text{dm}^3$ ),  $C_e$  is the concentration of ions remaining in solution at equilibrium (mg /  $\text{dm}^3$ ),  $V$  is the volume of ion solution used ( $\text{dm}^3$ ) and  $m$  is the mass of adsorbent.

## RESULTS AND DISCUSSION

In Table 1 is shown the chemical composition of Kamenica's (Kosovo) clay and it is observed that silica and alumina are the major constituents.

The experiments were conducted at different times and initial heavy metal ions concentrations.

**Table 1:** Chemical composition of clay.

Composition	% by weight
$\text{SiO}_2$	45.75
$\text{Al}_2\text{O}_3$	13.61
$\text{K}_2\text{O}$	8.01
$\text{MgO}$	7.70
$\text{Fe}_2\text{O}_3$	10.76
$\text{CaO}$	4.84
$\text{Na}_2\text{O}$	4.43

**Table 2:** Adsorption parameters for the adsorption of  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  on clays at different initiations concentration

Cu	$C_0$ (mg/ $\text{dm}^3$ )	$C_e$ (mg/ $\text{dm}^3$ )	$q_e$ (mg/g)	R %	$C_e/q_e$	$\ln C_e$	$\ln q_e$	$R_L$
Natural Clay	35.21	1.02	0.17	97.10	5.97	0.02	-1.77	0.02
	70.42	20.40	0.25	71.03	81.57	3.02	-1.39	0.01
	100.20	48.00	0.26	52.09	183.92	3.87	-1.34	0.01
Treated Clay	31.76	6.30	0.13	80.16	49.49	1.84	-2.06	0.16
	70.90	37.30	0.17	47.39	222.02	3.62	-1.78	0.08
	100.20	69.00	0.16	31.14	442.31	4.23	-1.86	0.06
Mn	$C_0$ mg/ $\text{dm}^3$	$C_e$ (mg/ $\text{dm}^3$ )	$q_e$ (mg/g)	R %	$C_e/q_e$	$\ln C_e$	$\ln q_e$	$R_L$
Natural Clay	36.40	2.84	0.168	92.198	16.925	1.04	-1.79	0.16
	69.94	6.94	0.315	90.076	22.033	1.94	-1.16	0.09
	98.97	15.84	0.416	83.995	38.109	2.76	-0.88	0.07
Treated Clay	37.20	6.75	0.152	81.854	44.338	1.91	-1.88	0.12
	68.83	31.00	0.189	54.961	163.891	3.43	-1.67	0.07
	99.80	55.00	0.224	44.888	245.552	4.01	-1.50	0.05

The adsorption was seen to increase rapidly at the initial stage and the equilibrium (maximum) adsorption was obtained in 60 minutes.

It is seen that the uptake capacity of the clay 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 and higher interaction between ions and adsorbent<sup>16</sup>.

Adsorption is described through functions which connect the amount of adsorbate on the adsorbent. Distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm models such as Langmuir and Freundlich. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface<sup>17</sup>.

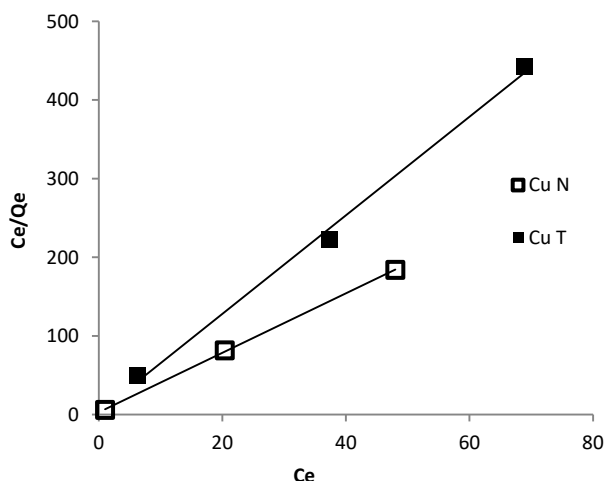
Once a site is filled, no further sorption can take place at that site. This indicates that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved. The isotherm is represented by equation 3.

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

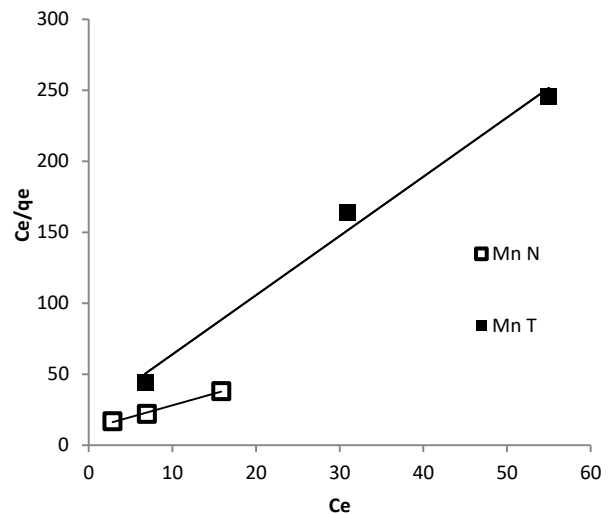
$C_e$  (mg/dm<sup>3</sup>) is the concentration of heavy metal ions in equilibrium,  $q_e$  (mg/g) is the equilibrium uptake capacity,  $q_m$  (mg/g) is the maximum adsorption capacity corresponding to a complete monolayer coverage and  $b$  (dm<sup>3</sup>/mg) is the Langmuir isotherm constant which quantitatively reflects the affinity between the adsorbent and the adsorbate.

The linear plot of specific adsorption  $C_e/q_e$  against the equilibrium concentration  $C_e$ , Figure 1 and 2 shows that the adsorption obeys the Langmuir model.

$Q_m$  and  $b$  were calculated from the slope and intercept respectively.



**Figure 1:** Langmuir's linear isotherms related to adsorption of Cu<sup>2+</sup> from aqueous solution on natural (Cu N) and treated clay (Cu T).



**Figure 2:** Langmuir's linear isotherms related to adsorption of Mn<sup>2+</sup> from aqueous solution on natural (Mn N) and treated clay (Mn T).

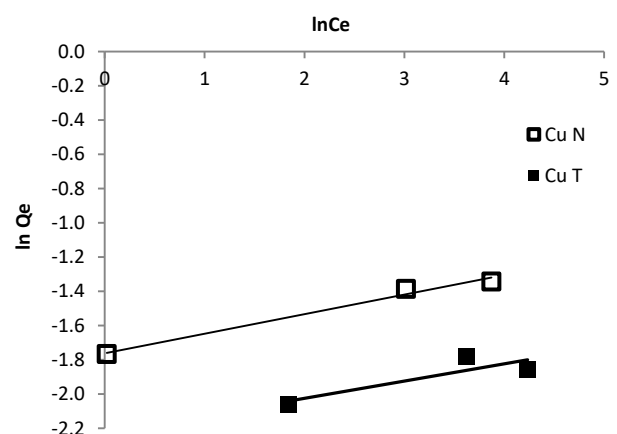
The Freundlich isotherm is introduced as an empirical model, where  $q_e$  represents the amount adsorbed per amount of adsorbent at the equilibrium (mg/g),  $C_e$  represents the equilibrium concentration (mg/dm<sup>3</sup>), and  $K_f$  and  $n$  are parameters that depend on the adsorbate and adsorbent<sup>18</sup>.

It is represented by the equation 4.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{4}$$

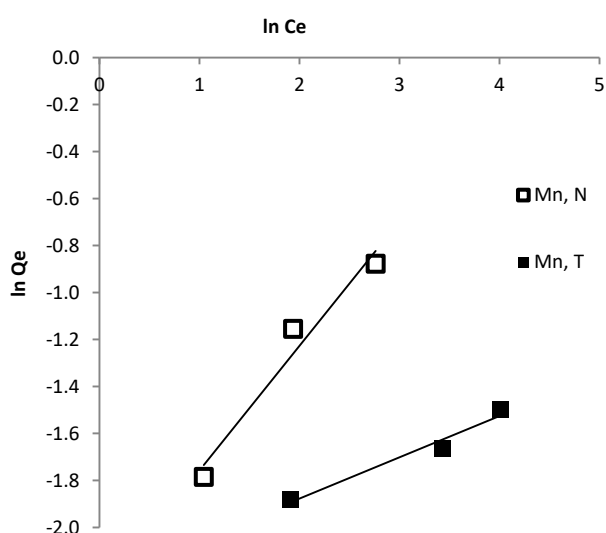
$n$  is a dimensionless constant describing the adsorption intensity and  $K_f$  (dm<sup>3</sup>/g) is the Freundlich isotherm constant describing the adsorption capacity of the adsorbent<sup>16</sup>.

The Freundlich isotherms were confirmed by the plot of  $\ln q_e$  against  $\ln C_e$  shown in Figure 3 and 4.



**Figure 3:** Freundlich's linear isotherms related to adsorption of Cu<sup>2+</sup> from aqueous solution on natural (Cu, N) and treated clay (Cu, T).

The Langmuir and Freundlich isotherm constants are given in Table 3.



**Figure 4:** Freundlich's linear isotherms related to adsorption of  $Mn^{2+}$  from aqueous solution on natural (Mn, N) and treated clay (Mn, T).

The value of  $b$  (Langmuir constant) obtained is low which implies that the sorption of  $Cu^{2+}$  and  $Mn^{2+}$  ions onto our clay is a favorable one. The Langmuir constant ranged between 0.14 and 1.27 for natural clay and 0.19 and 2.33 for treated clay shows that the adsorption was more favorable for the natural clay.

**Table 3:** Langmuir and Freundlich constants for the adsorption of  $Cu^{2+}$  and  $Mn^{2+}$  ions on clay.

Langmuir isotherm					
Clay	Metal ion	$q_m$	$b$	$R^2$	$R_L$
Natural	$Cu^{2+}$	0.26	1.27	0.9998	$0 < R_L < 1$
Treated	$Cu^{2+}$	0.16	2.33	0.9960	$0 < R_L < 1$
Natural	$Mn^{2+}$	0.60	0.14	0.9935	$0 < R_L < 1$
Treated	$Mn^{2+}$	0.24	0.19	0.9890	$0 < R_L < 1$
Freundlich isotherm					
Clay	Metal ion	$n$	$K_f$	$R^2$	
Natural	$Cu^{2+}$	8.75	0.17	0.9853	
Treated	$Cu^{2+}$	9.92	0.11	0.7609	
Natural	$Mn^{2+}$	1.88	0.10	0.9614	
Treated	$Mn^{2+}$	5.69	0.17	0.9664	

The dimensionless separation factor ( $R_L$ ), as a measure of the adsorption favorability, was calculated ( $0 < R_L < 1$ , the smaller is the more favorable) by using the following equation:  $R_L = 1/(1+bC_0)$  where  $b$  is the Langmuir constant<sup>19</sup>.

The  $n$  value in Freundlich equation was found to be 1.88–9.92. A value of  $n$  above unity indicates a favourable adsorption<sup>20</sup>. In the present study, since  $n$  lies between 1 and 10 it indicates the physical adsorption of metal ions onto clay.

The value of the regression coefficient ( $R^2$ ) of both models are close to the value of 1, but correlation coefficients for the Langmuir isotherm are closer to 1 and this shows that Langmuir adsorption isotherm was the better model for the metal ions adsorption onto our clay.

## CONCLUSIONS

The batch adsorption of  $Cu^{2+}$  and  $Mn^{2+}$  ions on Kosovo clay showed that the clay can be used as a cheap alternative adsorbent for removal of these ions from aqueous solutions.

The percentage of adsorption of  $Cu^{2+}$  and  $Mn^{2+}$  from aqueous solution onto Kosovo clay goes up to the value 97.10 %.

The adsorption process obeys both Langmuir and Freundlich adsorption isotherms.

It is clear from the results that adsorption of  $Cu^{2+}$  and  $Mn^{2+}$  on our clay was favorable.

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