

## Adsorption of Copper and Zinc from Aqueous Solutions by Bentonite

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Bentonite has been used as an adsorbent for the removal of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions from aqueous solutions *via* adsorption. The effect of the adsorbent amount, pH of suspension, solution concentration and temperature and the contact time on adsorption was investigated. The amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions adsorbed increased with increasing adsorbent amount, pH and temperature and with decreasing concentration. The adsorption parameters were obtained using Reciprocal Langmuir, Langmuir, Linear Freundlich, Freundlich and Langmuir-Freundlich isotherm models by use of non linear regression analysis. The adsorption isotherm studies indicated that adsorption was consistent with the Reciprocal Langmuir isotherm model. Results of the thermodynamic studies indicated that the adsorption of both ions on bentonite was spontaneous and favourable and an endothermic nature of adsorption. A pseudo-second order equation described the adsorption process for either  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$ . The results of this study demonstrated that the bentonite is a potential adsorbent for the removal of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions from aqueous solutions.

**Key Words:** Bentonite, Copper, Zinc, Adsorption, Kinetic, Isotherm.

### INTRODUCTION

A majority of metallic elements are toxic such as aluminium, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead, *etc.* The increasing contamination of water and wastewater by toxic metallic elements is a serious environmental problem<sup>1-3</sup>. The main industrial sources of toxic metallic element contamination in water and wastewater include electroplating, metal finishing, metallurgical, tannery, chemical manufacturing, mining and battery manufacturing industries and others<sup>4,5</sup>. The toxic metallic elements selected for removal in this study *e.g.*, copper and zinc, even in relatively low concentrations, can cause gastrointestinal distress, liver and

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kidney damage, anemia and several kinds of cancer<sup>6-8</sup>. Therefore, the removal of excess toxic metallic elements from water and wastewater is essential to protect human and environmental health. As a result, various physico-chemical and biological methods have been studied and developed for toxic metallic elements removal from aqueous solution<sup>9</sup>. Among the available physico-chemical treatment processes, adsorption has been found to be an effective and economical method with high potential for the removal, recovery and recycling of metals from wastewater<sup>10,11</sup>. The use of clays as an adsorbent to remove contaminants has been of increasing interest because they are cheaper than other materials such as activated carbon and zeolite<sup>12</sup>. A high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity, a tendency to hold water in the interlayer sites and the presence of Brønsted and Lewis acidity have made clays, especially smectite type clays, excellent adsorbent materials<sup>10,11</sup>. Therefore, a number of studies have been conducted using clays, to show their effectiveness for removing metal ions such as Cu(II), Zn(II), Pb(II), Cd(II), Fe(II), Ni(II), Co(II), Cr(III) from aqueous solution<sup>1-6,9,10,12-21</sup>. The removal of toxic metallic ions such as copper, zinc, lead and chromium ions from aqueous solution were tested by clays from Middle Anatolia<sup>22,23</sup>. However, the thermodynamic data of Cu<sup>2+</sup> and Zn<sup>2+</sup> adsorption on bentonite is comparatively less studied, particularly the effect of temperature on Cu<sup>2+</sup> and Zn<sup>2+</sup> adsorption is important to describe the adsorption mechanism of Cu<sup>2+</sup> and Zn<sup>2+</sup>.

The aim of this study is to investigate the effect of various important parameters such as adsorbent amount, pH of suspension, initial solution concentration and temperature and contact time on the adsorption capacity of Cu<sup>2+</sup> and Zn<sup>2+</sup> from aqueous solutions by raw bentonite from Middle Anatolia.

## EXPERIMENTAL

**Adsorbent and reagents:** As the adsorbent, bentonite from the Hancili region (Middle Anatolia, Turkey), called Hancili Green Bentonite (HGB) due to their appearance, was used. Characterization of this bentonite sample by chemical composition, X-ray diffraction, cation exchange capacity and BET surface area was reported elsewhere<sup>24,25</sup>. The some physico-chemical properties of this bentonite sample are given in Table-1.

TABLE-1  
PHYSICO-CHEMICAL PROPERTIES OF HGB SAMPLE

Metal oxides (%)		Metal oxides (%)	
SiO <sub>2</sub>	66.95	K <sub>2</sub> O	1.19
Al <sub>2</sub> O <sub>3</sub>	18.38	BET specific surface area (m <sup>2</sup> g <sup>-1</sup> )	76.80
Fe <sub>2</sub> O <sub>3</sub>	6.11	Basal spacing (d <sub>001</sub> ) nm (at room temperature)	1.24
MgO	2.75	CEC (cmol kg <sup>-1</sup> )	50.00
CaO	1.80	Colour	Green
Na <sub>2</sub> O	2.81		

All the necessary reagents used in this study were of analytical grade (Merck) and all solutions were prepared in deionized water. Stock  $1 \text{ g dm}^{-3}$  standard solutions of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions were prepared by dissolving appropriate amounts of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in deionized water. Working solutions of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  were prepared by appropriate dilutions of the stock solutions. Solutions of  $0.1 \text{ mol dm}^{-3}$  NaOH and  $\text{HNO}_3$  were used for pH adjustment.

**Adsorption experiments:** The adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions on the HGB was studied by batch technique. The batch adsorption experiments were carried out in  $50 \text{ cm}^3$  plastic bottle by mixing  $50 \text{ mg}$  HGB and  $25 \text{ cm}^3$  solution of metal ions and shaking the suspension in a thermostatic shaking water bath (Mettler) for 24 h at 298 K. After this period, the suspensions were filtered. Then the equilibrium concentration of metal ions in the filtrate was determined using flame atomic absorption spectrometer with air-acetylene flame (Perkin-Elmer AA800 Model AAS). The amount of metal ions adsorbed was calculated by the difference between the initial concentrations and the equilibrium concentrations of metal ions. All experiments were performed in duplicate using two independent samples, besides a blank sample and mean values were taken into account. The experiments were carried out by varying the amount of the adsorbent, pH of the suspension, initial concentration of metal ions, temperature and contact time.

The effect of amount of HGB on  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorption was investigated by changing the adsorbent amount from 2 to  $6 \text{ g dm}^{-3}$  with the initial  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentrations at  $0.472$  and  $0.459 \text{ mmol dm}^{-3}$  and shaking time of 24 h at 298 K. The effect of the pH of the suspension on the adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  on HGB was performed in the pH range of 1.6-7.0 for Cu and in the pH range of 1.5-9 for Zn with a constant HGB amount of  $2 \text{ g dm}^{-3}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  concentration of  $0.472$  and  $0.459 \text{ mmol dm}^{-3}$  and shaking time of 24 h at 298 K. The suspension pH was adjusted with  $0.1 \text{ M HNO}_3$  or  $0.1 \text{ M NaOH}$  solutions at the beginning of the experiment and not controlled afterwards. The effect of initial  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentrations on adsorption was investigated within the interval  $0.15$ - $4.72 \text{ mmol dm}^{-3}$  with a constant HGB amount of  $2 \text{ g dm}^{-3}$ , shaking time 24 h at 298, 313 and 333 K. The effect of contact time on adsorption was investigated by changing contact time from 5 to 1440 min with the initial  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentrations at  $0.472$  and  $0.459 \text{ mmol dm}^{-3}$  at 298 K. All the experiments (except pH effect) were carried out at pH of the sorptive solution. All pH measurements were performed with a WTW Inolab pH 720 model digital pH meter.

## RESULTS AND DISCUSSION

**Effect of amount of Hancili Green Bentonite (HGB):** The adsorbent amount as an important parameter determines the adsorption capacity of an adsorbent for a given initial concentration of the adsorbate. Effect of amount of HGB on  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorption is shown in Fig. 1, which showed that as the adsorbent amount increases, the amount of metal ions adsorbed per unit mass of adsorbent at equilibrium

( $n_e$ ) decreased. The amount of metal ions adsorbed was  $0.216 \text{ mmol g}^{-1}$  and  $0.190 \text{ mmol g}^{-1}$  at HGB  $2 \text{ g dm}^{-3}$ , decreased to  $0.078$  and  $0.073 \text{ mmol g}^{-1}$  at HGB  $6 \text{ g dm}^{-3}$ , for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , respectively. This was an expected result since as the amount of adsorbent increases, the saturation of the adsorption sites effectively reduces and, correspondingly, the number of such sites per unit mass comes down, resulting in relatively less adsorption. However, it was observed that the percentage adsorption of metal ions increased with increase in adsorbent amount. Thus, the percentage adsorption of metal ions as obtained as  $92.70$  and  $86.60 \%$  at HGB  $2 \text{ g dm}^{-3}$  increased to  $99.67$  and  $95.63 \%$  at HGB  $6 \text{ g dm}^{-3}$ , for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , respectively. The increased percentage adsorption of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions with increasing HGB amount can be attributed to increased adsorbent surface and availability of more adsorption sites. Similar conclusions have been reported for the removal of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  by clay-based adsorbents<sup>13,14,16,23</sup>.

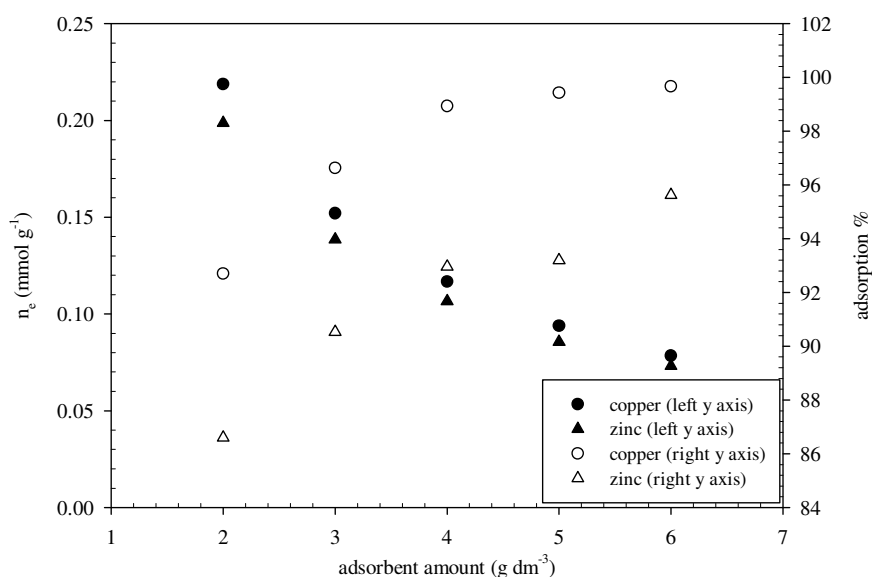


Fig. 1. Effect of the amount of adsorbent on amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorbed per unit mass of HGB and adsorption % (initial concentration of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ :  $0.472$  and  $0.459 \text{ mmol dm}^{-3}$ , temperature:  $298 \text{ K}$ )

**Effect of the pH:** An important parameter to be considered in adsorption process was the pH of the medium. The effect of suspension pH on the amount of metal ions adsorbed is presented in Fig. 2. It was observed that the amount of metal ions adsorbed per unit mass ( $n_e$ ) of HGB was influenced by the pH of the suspension and increased when the pH of the suspension was increased.  $n_e$  of the  $\text{Cu}^{2+}$  ions by the increase of pH from 1.6 to 7.0 increased from  $0.103$  to  $0.235 \text{ mmol g}^{-1}$ . Similar behaviour was observed in case of  $\text{Zn}^{2+}$ -clay interactions. At low pH values ( $\text{pH} < 3$ ), metal ions have to compete with the large number of  $\text{H}_3\text{O}^+$  ions for the surface sites

and as a result, the amount of metal ions adsorbed per unit mass was low. However, with increasing pH > 3, the competition from  $\text{H}_3\text{O}^+$  ions decreases and the metal ions can be adsorbed on the adsorbent<sup>6,9,14,16</sup>.

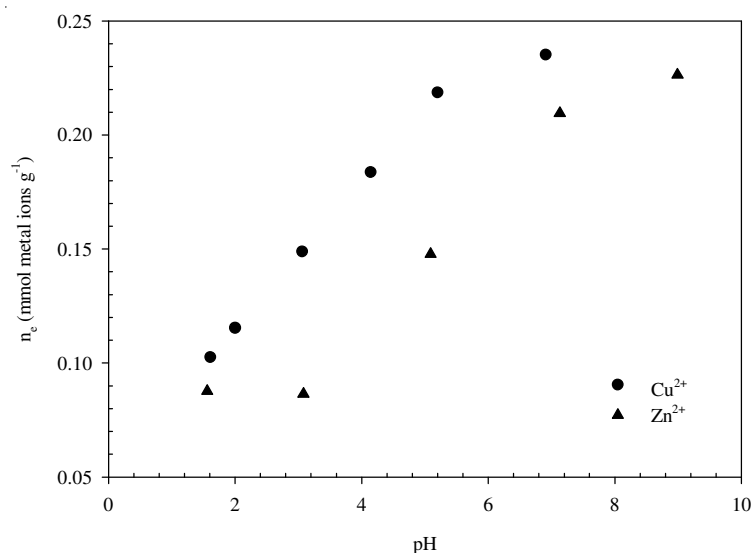


Fig. 2. Effect of pH of suspension on amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions adsorbed per unit mass of HGB (initial concentration of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ :  $0.472$  and  $0.459$   $\text{mmol dm}^{-3}$ , amount of HGB:  $2$   $\text{g dm}^{-3}$ , temperature:  $298$  K)

**Effect of initial  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentration:** Effect of initial  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentration on adsorption (%) and amount adsorbed per unit mass of HGB was summarized in Table-2. As the initial  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentration increased, the amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorbed per unit mass of HGB also increased, but the  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  percentage adsorption decreased (Table-2). The initial  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentrations were increased from  $0.15$  to  $4.7$   $\text{mmol dm}^{-3}$ , the amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorbed per unit mass of HGB increased from  $0.078$  to  $0.481$   $\text{mmol g}^{-1}$  for  $\text{Cu}^{2+}$  and  $0.075$  to  $0.451$   $\text{mmol g}^{-1}$  for  $\text{Zn}^{2+}$  at  $298$  K, however the  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorption percentages decreased from  $98.95$  to  $20.38$  % for  $\text{Cu}^{2+}$  and  $97.70$  to  $19.67$  % for  $\text{Zn}^{2+}$ .

**Adsorption isotherms:** The adsorption isotherm represents the relationship between the amount adsorbed by a unit mass of solid sorbent and the amount of solute remaining in the solution at equilibrium. Adsorption isotherms of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions from aqueous solution on the HGB at  $298$ ,  $313$  and  $333$  K are shown in Fig. 3. It was obtained that the amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorbed per unit mass of HGB increased with a rise in temperature. The degree of adsorption increases with increased temperature, indicating that the adsorption is endothermic process. Bereket *et al.*<sup>26</sup> reported that the amount of  $\text{Pb(II)}$ ,  $\text{Cd(II)}$ ,  $\text{Cu(II)}$  and  $\text{Zn(II)}$  adsorbed onto bentonite decreased with increasing temperature.

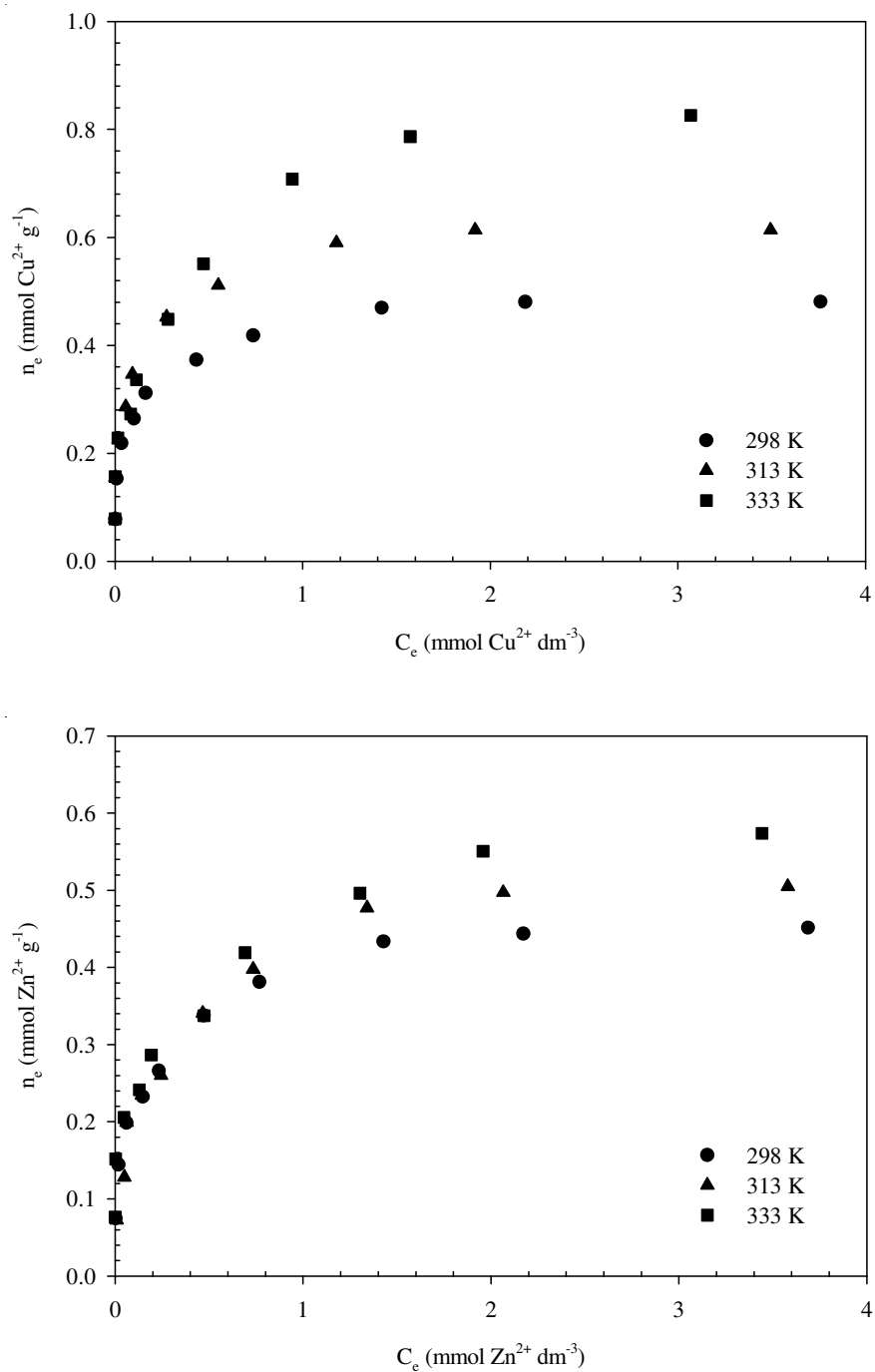


Fig. 3. Effect of initial  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions concentration on amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions adsorbed per unit mass of HGB (HGB amount:  $2 \text{ g dm}^{-3}$ , temperature: 298, 313 and 333 K)

TABLE-2  
EFFECT OF INITIAL  $\text{Cu}^{2+}$  AND  $\text{Zn}^{2+}$  IONS CONCENTRATION ON ADSORPTION (%)  
AND AMOUNT ADSORBED PER UNIT MASS OF HGB FOR ADSORPTION OF  
 $\text{Cu}^{2+}$  AND  $\text{Zn}^{2+}$  (HGB AMOUNT:  $2 \text{ g dm}^{-3}$ , TEMPERATURE: 298 K)

$C_o$ ( $\text{mmol dm}^{-3}$ )	$\text{Cu}^{2+}$		$C_o$ ( $\text{mmol dm}^{-3}$ )	$\text{Zn}^{2+}$	
	$n_e$ ( $\text{mmol g}^{-1}$ )	Adsorption (%)		$n_e$ ( $\text{mmol g}^{-1}$ )	Adsorption (%)
0.157	0.078	98.95	0.153	0.075	97.70
0.315	0.153	97.40	0.306	0.144	94.30
0.472	0.219	92.70	0.459	0.190	82.90
0.629	0.264	83.98	0.612	0.233	75.98
0.787	0.312	79.26	0.765	0.267	69.54
1.180	0.373	63.28	1.147	0.338	58.88
1.574	0.418	53.18	1.530	0.381	49.84
2.360	0.470	39.79	2.295	0.434	37.79
3.147	0.481	30.54	3.060	0.444	29.00
4.721	0.481	20.38	4.589	0.451	19.67

To optimize the design of an adsorption system to remove  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions from aqueous solutions, it is important to establish the most appropriate correlation for the equilibrium curve. Therefore, the experimental adsorption data were analyzed with Reciprocal Langmuir, Langmuir, Linear Freundlich, Freundlich and Langmuir-Freundlich isotherm equations by use of non-linear regression analysis. These isotherm equations were represented as follows eqns. 1-5<sup>5,13,15,27</sup>.

$$\frac{C_e}{n_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (1) \text{ (Reciprocal Langmuir, Rec. L)}$$

$$n_e = \frac{K_L C_e q_m}{(1 + K_L C_e)} \quad (2) \text{ (Langmuir, L)}$$

$$\log n_e = \log K_F + \frac{1}{n} \log C_e \quad (3) \text{ (Linear Freundlich, Lin. F)}$$

$$n_e = K_F C_e^{\frac{1}{n}} \quad (4) \text{ (Freundlich, F)}$$

$$n_e = \frac{q_m K_{LF} C_e^{\frac{1}{n}}}{(1 + K_{LF} C_e^{\frac{1}{n}})} \quad (5) \text{ (Langmuir-Freundlich, L-F)}$$

In these equations,  $C_e$  ( $\text{mmol dm}^{-3}$ ) and  $n_e$  ( $\text{mmol g}^{-1}$ ) are the equilibrium concentration of metal ions in the liquid phase and in the solid phase.  $K_L$  ( $\text{dm}^3 \text{ mmol}^{-1}$ ) and  $q_m$  ( $\text{mmol g}^{-1}$ ) are the Langmuir constant and the monolayer adsorption capacity ( $\text{mmol g}^{-1}$ ).  $K_F$  ( $\text{dm}^3 \text{ mmol}^{-1}$ ) and  $n$  are isotherm constants representing the adsorption capacity and the degree of non-linearity between solution concentration and adsorption, respectively.  $K_{LF}$  ( $\text{g mmol}^{-1}$ ) is Langmuir-Freundlich constant.

The adsorption data were analyzed according to the Reciprocal Langmuir isotherm (eqn. 1). The values of the Langmuir constants  $q_m$  and  $K_L$  with the correlation coefficient are presented in Table-3. Reciprocal Langmuir isotherms are shown in Figs. 4 and 5 together with the experimental data points for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  at three different temperatures. The values of correlation coefficient are higher than the other four isotherm values for both  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ .  $q_m$  and  $K_L$  values for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  were found to be  $0.48 \text{ mmol g}^{-1}$ ,  $20.45 \text{ dm}^3 \text{ mmol}^{-1}$  and  $0.45 \text{ mmol g}^{-1}$ ,  $12.15 \text{ dm}^3 \text{ mmol}^{-1}$ , respectively.

TABLE-3  
ADSORPTION ISOTHERM CONSTANTS AND CORRELATION  
COEFFICIENTS FOR THE ADSORPTION OF  $\text{Cu}^{2+}$  AND  $\text{Zn}^{2+}$   
IONS ON HGB AT DIFFERENT TEMPERATURES

Temp. (K)	Reciprocal Langmuir			Langmuir		Linear Freundlich			Freundlich			Langmuir- Freundlich		
	$q_m$	$K_L$	$R^2$	$K_L$	$R^2$	$K_F$	n	$R^2$	$K_F$	n	$R^2$	$K_{LF}$	n	$R^2$
$\text{Cu}^{2+}$														
298	0.48	20.45	0.998	16.40	0.922	0.02	4.55	0.971	0.41	5.26	0.978	6.89	1.64	0.972
313	0.61	22.73	0.999	16.60	0.933	0.05	4.76	0.989	0.53	5.26	0.979	6.96	1.59	0.965
333	0.83	9.15	0.990	5.70	0.921	0.10	4.76	0.963	0.65	3.85	0.977	4.25	1.30	0.930
$\text{Zn}^{2+}$														
298	0.45	12.15	0.997	9.23	0.935	0.02	3.85	0.973	0.37	4.55	0.976	5.55	1.45	0.966
313	0.51	8.25	0.995	6.26	0.961	0.06	3.03	0.959	0.40	3.70	0.966	5.09	1.16	0.967
333	0.57	7.47	0.989	5.31	0.883	0.01	5.56	0.958	0.44	4.35	0.978	5.48	1.54	0.909

The adsorption data were also analyzed according to the nonlinear form of the Langmuir isotherm (eqn. 2). The values of the Langmuir constant  $K_L$  with the correlation coefficient for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  are listed in Table-3 and Langmuir isotherms are shown in Figs. 4 and 5. The values of correlation coefficient are lower than the other four isotherm values for both  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ .  $K_L$  values for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  were found to be  $16.40$  and  $9.23 \text{ dm}^3 \text{ mmol}^{-1}$ , respectively.

The adsorption data were analyzed according to linear form of the Freundlich isotherm (eqn. 3). The values of isotherm constants are listed in Table-2 and linear Freundlich isotherms are shown in Figs. 4 and 5 for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ . The correlation coefficient is higher than Langmuir value but lower than the Reciprocal Langmuir and non-linear Freundlich isotherm values for  $\text{Cu}^{2+}$  at 298 K. The correlation coefficient is higher than Langmuir and Langmuir-Freundlich isotherm values but lower than the other two isotherm values for  $\text{Zn}^{2+}$  at 298 K.  $K_F$  and exponent n values were obtained to be  $0.02 \text{ dm}^3 \text{ mmol}^{-1}$ ,  $4.55$  and  $0.02 \text{ dm}^3 \text{ mmol}^{-1}$ ,  $3.85$  for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , respectively.

The adsorption data were also analyzed according to non-linear form of the Freundlich isotherm (eqn. 4). The values of isotherm constants are listed in Table-2 and non-linear Freundlich isotherms are shown in Figs. 4 and 5 for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ . The correlation coefficient is lower than Reciprocal Langmuir isotherm value but



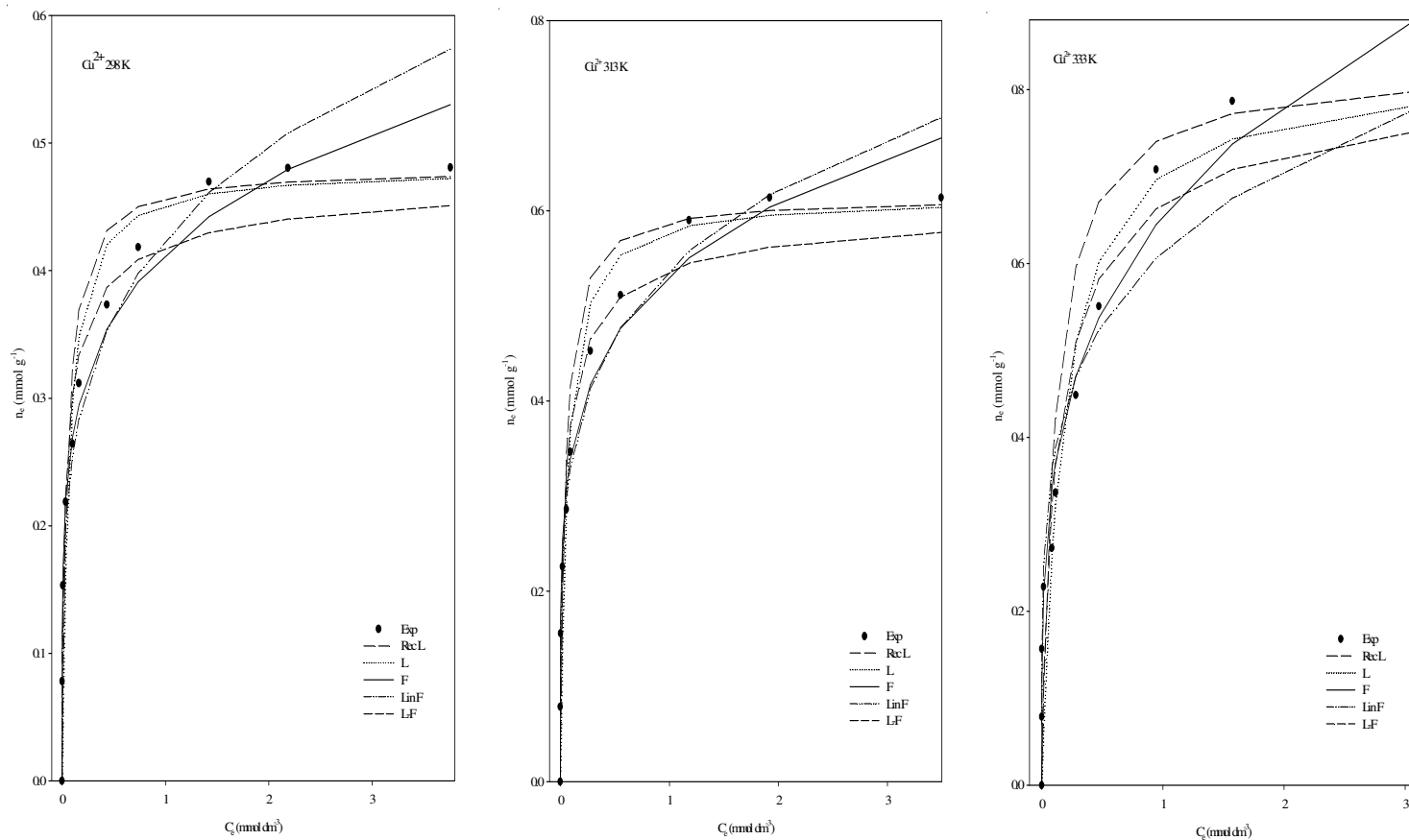


Fig. 4. Adsorption isotherms for adsorption of  $\text{Cu}^{2+}$  on HGB at different temperatures (initial concentration of  $\text{Cu}^{2+}$ : 0.158-4.721 mmol dm<sup>-3</sup>, HGB amount: 2 g dm<sup>-3</sup>)

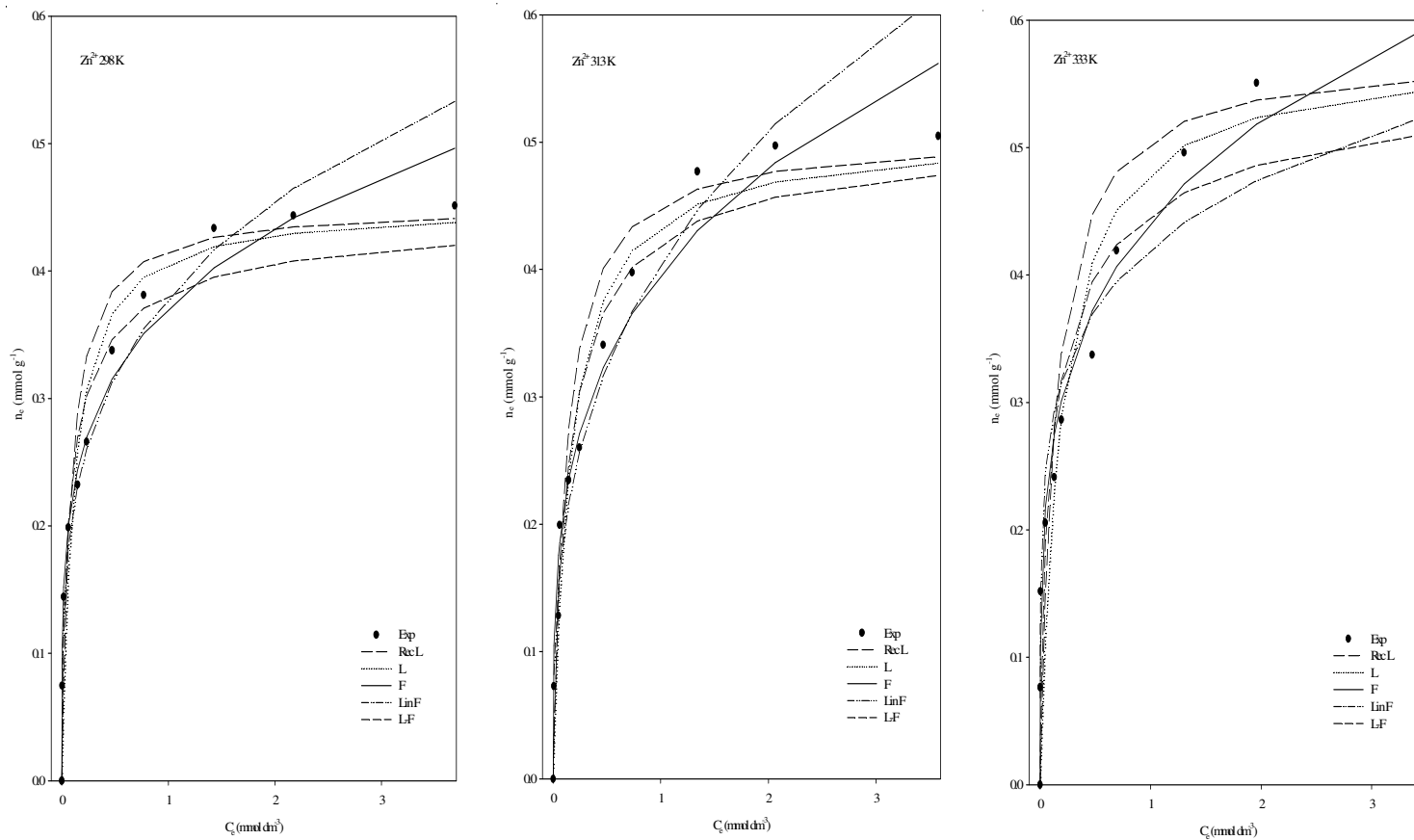


Fig. 5. Adsorption isotherms for adsorption of  $Zn^{2+}$  on HGB at different temperatures (initial concentration of  $Zn^{2+}$ : 0.153-4.589 mmol dm<sup>-3</sup>, HGB amount: 2 g dm<sup>-3</sup>)

higher than other three isotherm values for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  at 298 K. Non-linear Freundlich isotherm constant  $K_F$  and exponent  $n$  values were obtained to be  $0.41 \text{ dm}^3 \text{ mmol}^{-1}$ ,  $5.26$  and  $0.37 \text{ dm}^3 \text{ mmol}^{-1}$ ,  $4.55$  for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , respectively.

Langmuir-Freundlich isotherm constants are calculated and given in Table-3. Langmuir-Freundlich isotherms are shown in Figs. 4 and 5 together with the experimental data points. The correlation coefficients were also determined and are shown in Table-3. The value of correlation coefficient is higher than Langmuir and Linear Freundlich isotherm values but lower than other two isotherm values for  $\text{Cu}^{2+}$  at 298 K. The value of correlation coefficient is higher than Langmuir value but lower than other three isotherm values for  $\text{Zn}^{2+}$  at 298 K. The values of  $K_{LF}$  and exponent  $n$  values were obtained to be  $6.89 \text{ dm}^3 \text{ mmol}^{-1}$ ,  $1.64$  and  $5.55 \text{ dm}^3 \text{ mmol}^{-1}$ ,  $1.45$  for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , respectively.

As seen from Table-3 and Figs. 4 and 5, the reciprocal Langmuir isotherm provides the best correlation for the experimental adsorption data, whereas all isotherms show adequate fits of experimental data in the low equilibrium solution concentrations ( $< 0.2 \text{ mmol dm}^{-3}$ ).

**Adsorption thermodynamics:** The amount of adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions by HGB clay is measured in a temperature range 298-333 K. Thermodynamic parameters, Gibbs free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) for the adsorption process were calculated using the following equations<sup>6,22,28</sup>.

$$\Delta G = -RT \ln K_d \quad (6)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

where,  $R$  is the ideal gas constant ( $8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$ ),  $T$  is temperature (K) and  $K_d$  is the distribution coefficient of the adsorbate ( $= n_s/C_e$  in  $\text{dm}^3 \text{ g}^{-1}$ ). The enthalpy change ( $\Delta H$ ,  $\text{kJ mol}^{-1}$ ) and the entropy change ( $\Delta S$ ,  $\text{kJ mol}^{-1} \text{ K}^{-1}$ ) are determined (Table-4) from the slope and the intercept of the linear plot of  $\ln K_d$  versus  $1/T$ . The free energy change ( $\Delta G$ ) was calculated to be  $-4.58 \text{ kJ mol}^{-1}$  for  $\text{Cu}^{2+}$  and  $-2.91 \text{ kJ mol}^{-1}$   $\text{Zn}^{2+}$  at 298 K. The negative values of  $\Delta G$  mean that the adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions on HGB clay is spontaneous and thermodynamically favourable. The values of  $\Delta H$  and  $\Delta S$  were  $19.21 \text{ kJ mol}^{-1}$  and  $0.08 \text{ kJ mol}^{-1} \text{ K}^{-1}$  for  $\text{Cu}^{2+}$  as well as  $7.09 \text{ kJ mol}^{-1}$  and  $0.03 \text{ kJ mol}^{-1} \text{ K}^{-1}$  for  $\text{Zn}^{2+}$ . The values of  $\Delta H$  for the adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions on HGB is positive, indicating that the process is endothermic in nature. The positive values of entropy show increased disorder at the solid-solution interface during the adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions. Similar results were reported by Bhattacharyya and Gupta<sup>6</sup> and Eren and Afsin<sup>5</sup>. They reported the positive  $\Delta H$  and  $\Delta S$  values for adsorption of  $\text{Cu}^{2+}$  on clay-based adsorbents. However, Kubilay *et al.*<sup>15</sup>, Bereket *et al.*<sup>26</sup> and Guerra *et al.*<sup>28</sup> observed the negative value for adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  on bentonite and kaolinite.

TABLE-4  
DISTRIBUTION COEFFICIENT VALUES AND THERMODYNAMIC PARAMETERS  
FOR THE ADSORPTION OF  $\text{Cu}^{2+}$  AND  $\text{Zn}^{2+}$  IONS ON HGB AT DIFFERENT  
TEMPERATURES (INITIAL CONCENTRATION OF  $\text{Cu}^{2+}$  AND  
 $\text{Zn}^{2+}$ : 0.472 AND 0.459  $\text{mmol dm}^{-3}$ , HGB AMOUNT: 2  $\text{g dm}^{-3}$ )

Temp. (K)	$K_d$ ( $\text{dm}^3 \text{g}^{-1}$ )		$-\Delta G$ ( $\text{kJ mol}^{-1}$ )		$\Delta H$ ( $\text{kJ mol}^{-1}$ )		$\Delta S$ ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )	
	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$
298	6.35	3.23	4.58	2.91	19.21	7.09	0.08	0.03
313	11.31	3.31	6.31	3.11				
323	12.77	3.94	6.84	3.68				
333	14.35	4.31	7.38	4.04				

**Adsorption kinetic:** Fig. 6 shows the effect of contact time on the amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorbed per unit mass ( $n_t$ ) at 298 K. According to Fig. 6, the amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions adsorbed per unit mass of HGB rapidly increased in the first 5 min. After a rapid adsorption, the equilibrium was attained within 6 h for  $\text{Cu}^{2+}$  and 5 h for  $\text{Zn}^{2+}$ . The increase was not significant after 6 h for  $\text{Cu}^{2+}$  and 5 h for  $\text{Zn}^{2+}$ .

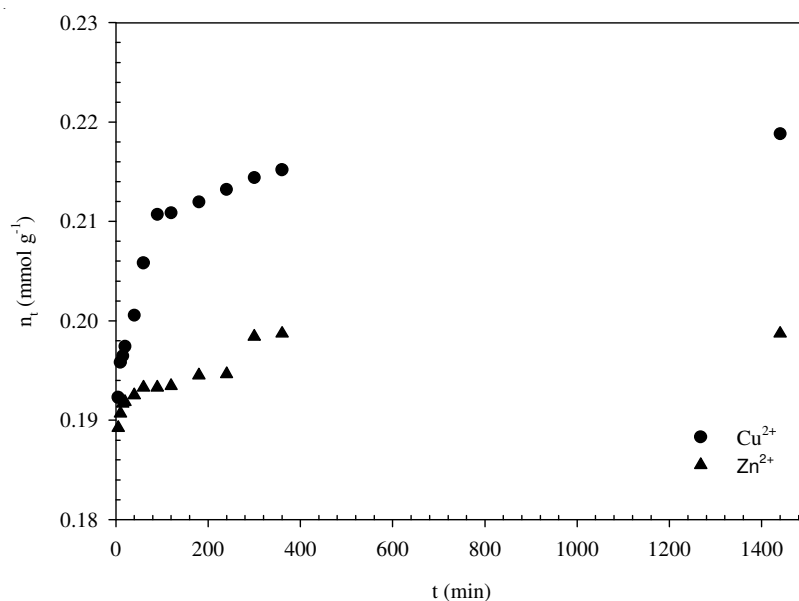


Fig. 6. Effect of the contact time on the amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorbed per unit mass of HGB (initial concentration of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ : 0.472 and 0.459  $\text{mmol dm}^{-3}$ , HGB amount: 2  $\text{g dm}^{-3}$ , temperature: 298 K)

In this study, Lagergren pseudo-first order equation and pseudo-second order equation were analyzed to find out which model is in agreement with the experimental data of kinetic study. The data were not fit well by the Lagergren pseudo-first order equation, as there were a poor correlation coefficient and the calculated amount of

adsorption ( $n_{e\text{-cal}}$ ) was far from the experimentally determined adsorption equilibrium ( $n_{e\text{-exp}}$ ). Therefore, the pseudo-second order rate equation was evaluated from the experimental data to determine the rate of adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  onto the HGB. The pseudo-second order equation is based on the adsorption capacity of the solid phase. The pseudo-second order kinetic model can be given as<sup>6,29</sup>:

$$\frac{t}{n_t} = \frac{1}{k_2 n_e^2} + \frac{t}{n_e} \quad (8)$$

where  $n_e$  ( $\text{mmol g}^{-1}$ ) is the amount of metal adsorbed at equilibrium,  $n_t$  ( $\text{mmol g}^{-1}$ ) is the amount adsorbed at time  $t$  (min),  $k_2$  is the adsorption rate constant pseudo-second order adsorption ( $\text{g mmol}^{-1} \text{min}^{-1}$ ). The value of  $k_2$  was determined from the slope of the plots of  $t/n_t$  versus  $t$  are given in Table-5. The pseudo-second order rate constants  $k_2$  for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorption on HGB were found to be 2.733 and 6.132  $\text{g mmol}^{-1} \text{min}^{-1}$ , respectively at 298 K. The calculated amount of adsorption ( $n_{e\text{-cal}}$ ) was similar to the experimental amount of adsorption equilibrium ( $n_{e\text{-exp}}$ ) (Table-5). The correlation coefficients for the linear plot were over 0.99 in present experimental systems.

TABLE-5  
KINETIC PARAMETERS FOR THE ADSORPTION OF  $\text{Cu}^{2+}$  AND  $\text{Zn}^{2+}$  IONS ON HGB  
(INITIAL CONCENTRATION OF  $\text{Cu}^{2+}$  AND  $\text{Zn}^{2+}$ : 0.472 AND 0.459  $\text{mmol dm}^{-3}$ ,  
HGB AMOUNT: 2  $\text{g dm}^{-3}$ ; TEMPERATURE: 298 K)

Cation	$n_{e\text{-exp}}$ ( $\text{mmol g}^{-1}$ )	Pseudo-second-order		
		$n_{e\text{-cal}}$ ( $\text{mmol g}^{-1}$ )	$k_2$ ( $\text{g mmol}^{-1} \text{min}^{-1}$ )	$R^2$
$\text{Cu}^{2+}$	0.215	0.216	2.733	0.999
$\text{Zn}^{2+}$	0.199	0.197	6.132	0.999

## Conclusion

The results of this study demonstrated that the Hancili Green Bentonite (HGB) is a potential adsorbent for the removal of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions from aqueous solutions. The adsorption process was shown to be affected by experimental conditions, such as adsorbent amount, pH of suspension, initial  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions concentration, temperature and contact time. The amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions adsorbed per unit mass was influenced by the pH of the suspension and increased when the pH of the suspension was increased. The values of the amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorbed per unit weight of HGB increased and adsorption % of the  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions decreased with the increase in the initial  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions concentration. The amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorbed per unit mass of HGB increased with an increase in temperature and the positive enthalpy value of the process showed that the adsorption process was endothermic. The Reciprocal Langmuir isotherm model was found to be in good agreement with the experimental data. The adsorption kinetic was fit to a pseudo second-order model. Using the model, it is found that the calculated adsorption equilibrium ( $n_{e\text{-cal}}$ ) was similar to the actual experimental adsorption equilibrium ( $n_{e\text{-exp}}$ ).

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