

Equilibrium and Kinetics Characteristics of Copper (II) Sorption onto Gytija

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Abstract The sorption characteristics of gytija to remove copper (Cu^{2+}) ions from aqueous solutions were satisfactorily described with the Freundlich, Langmuir and Dubinin–Redushckevich (D–R) models. The sorption capacity (q_{max}) of gytija was 11.76 mg g^{-1} . The D–R model indicated that the sorption of Cu^{2+} by gytija was almost taken place by chemisorption. Thermodynamic parameters such as change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) suggested that the adsorption process of Cu^{2+} by gytija was feasible, spontaneous and endothermic in nature. Kinetic examination of the equilibrium data showed that the sorption processes of Cu^{2+} ions followed well pseudo-second-order kinetics model.

Keywords Gytija · Copper · Thermodynamics · Kinetics

High levels of Cu^{2+} ions in the environment are harmful for many life forms. The sorption of metal ions from wastewaters or aqueous solutions has been studied using various sorbents such as zeolite, bentonite, peat, lignin, and chitin (Bailey et al. 1999). Metal ion adsorption by peat may take place via several mechanisms such as ion-exchange, surface adsorption, chemisorption, complexation, and adsorption–complexation, and it is believed that ion-exchange is the most prevalent mechanism (Sarı et al. 2007). Carbonate minerals are also effective removing heavy metals from aqueous solutions with a combination of

the mechanisms of ion-exchange and precipitation (García-Sánchez and Álvarez-Ayuso 2002).

Although there are many studies in literature on the removal of Cu^{2+} from aqueous solutions using different materials, low-cost and locally available natural materials such as gytija, which is a calcareous peat material found as partings in multi-layer coal deposits of Coal Basins, requires individual research. Gytija is a sapropelic formation which is black or brown mud with organic matter and has many gastropod shells (Ural and Yuksel 2004). The gytija layer, which is not used in the coal-power plant due to its low quality, must be removed before mining the underlying lignite layers. The aims of this study were to investigate the sorption characteristics of Cu^{2+} ions from aqueous solutions using gytija with regard to adsorption isotherms, kinetics and thermodynamics at different initial concentrations and temperatures.

Materials and Methods

The material used in this study was obtained from the Afşin-Elbistan Coal Basin of Turkey which has multi-layer coal deposits with clay and calcareous gytija partings. The gytija sample was oven dried at 105°C for 24 h and grounded through a $63 \mu\text{m}$ sieve. The studied gytija material had 26.9% organic matter, neutral pH (7.01), and 57.61% CaCO_3 . The more detailed composition of gytija was reported as 11.87% SiO_2 , 0.05% TiO_2 , 6.42% Al_2O_3 , 0.69% Fe_2O_3 , 1.81% MgO , 17.44% CaO , 0.88% Na_2O , 0.44% K_2O , and 61.30% loss on ignition (Ural and Yuksel 2004).

Experiments of thermodynamics and kinetics were studied for 9.53, 19.05, and 38.10 mg L^{-1} Cu^{2+} ion concentrations at 25, 30, and 35°C . Copper stock

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solutions were prepared using analytical grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The effect of various solution pH on Cu^{2+} sorption by gyttja was studied, and the value of optimum solution pH was selected as 5.3 to avoid the formation of precipitate and obtain free metal ions in solution (Chamarthy et al. 2001). The thermodynamic and kinetic studies were conducted in a temperature controlled-agitated sorber vessel containing 500 mL solution and 2 g of gyttja sample. Sub-samples (5 mL) were taken at suitable time intervals up to 180 min, filtered and analyzed for Cu^{2+} ions. For the batch sorption studies 0.4 g gyttja sample was weighted into a 125 mL erlenmeyer flask, and 50 mL solution containing 19.05–95.25 mg L^{-1} Cu^{2+} ions were added into each flask. The sorption experiments were run in duplicates. For maximum Cu^{2+} ion removal, the flasks were shaken for 3 h (the equilibrium time) at $21 \pm 1^\circ\text{C}$ and filtered with whatman no. 42 filter paper. Metal ion concentrations were determined using an atomic absorption spectrometer (Perkin Elmer 3110). The amount of Cu^{2+} ions sorbed by gyttja was calculated by the difference between the initial and equilibrium concentrations of the solutions. The mean value of the duplicate analysis was used to calculate the amount of Cu^{2+} in solution, and the limit of error of duplicate samples was lower than 5%.

Results and Discussion

The sorption isotherms explain the specific relation between the concentration of a sorbate and its sorption degree onto a sorbent under different conditions. The sorption capacities of gyttja for Cu^{2+} ions were evaluated using Langmuir and Freundlich isotherms. The linear form of the Langmuir model is as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (1)$$

where C_e is the equilibrium concentration of Cu^{2+} ions in solution (mg L^{-1}), q_e is the amount of sorbed metal ion (mg g^{-1}) by per unit mass of gyttja (g), q_{\max} is maximum sorption capacity (mg g^{-1}), and K_L represents sorption energy coefficient (L mg^{-1}). The plot of C_e/q_e versus C_e yielded a straight line with a high coefficient of determination value ($R^2 = 0.940$), indicating that the equilibrium data fit to the Langmuir model. The maximum Cu^{2+} sorption (q_{\max}) onto gyttja and the sorption energy coefficient (K_L), which were calculated from the slope and the intercept of the linear plot, were 11.76 mg g^{-1} and 0.091 L mg^{-1} at 21°C , respectively. The comparison of gyttja with various adsorbents in terms of sorption capacity for Cu^{2+} ions from aqueous solution is given in Table 1. Gytja is very competitive for the removal of Cu^{2+} ions from

Table 1 Comparison of gyttja with various adsorbent materials for Cu^{2+} sorption

Adsorbent	q_{\max} (mg g^{-1})	References
Gyttja	11.76	Present study
Modified peanut husk	10.15	Li et al. (2007)
Sawdust	6.6	Li et al. (2007)
Herbaceous peat	4.84	Gündoğan et al. (2004)
Expanded perlite	8.62	Sari et al. (2007)
Natural zeolite	8.90	Erdem et al. (2004)
Activated poplar sawdust	13.50	Acar and Eren (2006)

aqueous solutions and wastewaters compared with the different adsorbents in the literature.

The adsorption data were applied to the Freundlich model in the logarithmic form (Eq. 2):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

In this equation, K_f is a constant related to the adsorption capacity (mg g^{-1}), and $1/n$ is a constant relating to adsorption intensity or surface heterogeneity (L g^{-1}). The determination coefficient (R^2) value of the linear plot of Freundlich isotherm was 0.997. The K_f and $1/n$ parameters for Freundlich model were 1.56 and 0.52, respectively. The Freundlich constants K_f and $1/n$ for Sphagnum peat for Cu^{2+} ions at pH 5.6 were reported as 2.88 and 0.68, respectively (Kalmykova et al. 2008). The magnitude of $1/n$ value generally ranges from 0 to 1, and it is a measure of exchange intensity or surface heterogeneity, and the value of $1/n$ smaller than 1 is accepted as an indicator of favourable removal conditions (Ho et al. 2002). The sorption data was better described with the Freundlich model ($R^2 = 0.997$) compared to the Langmuir model ($R^2 = 0.940$) based on the coefficient of determination (R^2) values. The better fit or the higher coefficient of determination value of the Freundlich model compared with the Langmuir model can be explained with the existence of heterogeneous surfaces for sorption (Sparks 1995) on gyttja (calcareous peat materials).

The equilibrium data were also applied to the Dubinin–Redushkevich (D–R) model to determine the nature of sorption processes whether it is physical or chemical. The linear form of the D–R isotherm equation (Dubinin et al. 1947) is shown in Eq. 3:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (3)$$

where q_e is the amount of metal ion adsorbed on per unit weight of gyttja (mol L^{-1}), q_m is the maximum sorption capacity (mol g^{-1}), β is the activity coefficient related to mean sorption energy ($\text{mol}^2 \text{J}^{-2}$), and ε is the Polanyi potential (Eq. 4).

$$\varepsilon = RT \ln(1 + 1/C_e) \tag{4}$$

The nature of the sorption mechanism can be determined with the mean free energy of sorption (*E*), which is calculated by the following equation:

$$E = 1/\sqrt{-2\beta} \tag{5}$$

The *q_m* value was found to be 7.24×10^{-4} mol g⁻¹. As mentioned before, the mean free energy of sorption gives information about the nature of the sorption mechanism. If *E* value lies between 9 and 16 kJ mol⁻¹, the sorption process is accepted to take place chemically. The sorption process is physical, however, if *E* value is smaller than 8 kJ mol⁻¹ (Dubinin et al. 1947; Saltali et al. 2007; Donat et al. 2005). The equilibrium data were fitted well to the D–R isotherm model (*R*² = 0.991). The mean sorption energy was calculated as 10.25 kJ mol⁻¹, which indicated that the sorption of Cu²⁺ onto gyttja was essentially chemical. It is likely that negatively charged surface functional groups form coordinate bonds with positively charged Cu²⁺ ions, and Cu²⁺ ions are immobilized as predominately inner sphere complex on binding sites because of ligands surrounding Cu²⁺ (Bloom and McBride 1979). The Cu²⁺ sorption is believed to differ from other metals, and Cu²⁺ ions with high-spin configuration have strong tendency to form stable complexes with peat (Kalmykova et al. 2008). Bloom and McBride (1979) reported that because of Jahn–Teller distortion, the d electrons in Cu²⁺ ions are not spherically symmetrical, and one axis is different in length than the other two axes. Therefore, ligands surrounding Cu²⁺ ions are not in perfect octahedral symmetry. Because of these two different positions (unsymmetrical position), Cu²⁺ ions are specifically adsorbed by the binding sites. Moreover, the materials high in the carbonate content can be associated with Cu²⁺ ions, probably due to occlusion and strong sorption (Spósito et al. 1982).

The effect of temperature on the sorption of Cu²⁺ ions by gyttja, and the distribution coefficient (*K_d*) was investigated at the temperatures of 25, 30 and 35°C by using Eq. 6.

$$K_d = \frac{q_e}{C_e} \tag{6}$$

where *q_e* (mg g⁻¹) and *C_e* (mg L⁻¹) are the equilibrium concentration of the Cu²⁺ ions on the sorbent and in solution, respectively. The *K_d* values were calculated for the temperatures of 25, 30 and 35°C (Table 2). The *K_d* values decreased as the initial Cu²⁺ ion concentrations increased, indicating higher uptake efficiency at lower Cu²⁺ ion concentrations.

In order to examine the thermodynamic behavior of the sorption of Cu²⁺ ions by gyttja, the enthalpy change (ΔH) and the entropy change (ΔS) were calculated from the slope and the intercept of the plots of log *K_d* versus 1/*T*.

$$\log K_d = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \tag{7}$$

The other thermodynamic parameter, Gibbs free energy change (ΔG°), was calculated using the following equation:

$$\Delta G^\circ = -RT \ln K_d \tag{8}$$

where ΔG° is free energy change (kJ mol⁻¹), *T* is temperature in Kelvin, and *R* is the gas constant (8.314 J mol⁻¹ K⁻¹). Gibbs free energy change at initial concentrations of 9.53 and 19.05 mg L⁻¹ suggested that the process was spontaneous and feasible with high preference for Cu²⁺ by gyttja (Table 2). The values of ΔG° calculated for initial concentration of 9.53 and 19.05 mg L⁻¹ at the same temperature increased. However, it had positive values when the initial concentration was 38.10 mg L⁻¹. These results implied that adsorption tendency of Cu²⁺ ions onto gyttja decreased as expected at high initial concentrations (Gündoğan et al. 2004; Sarı and Tuzen 2008).

The enthalpy change (ΔH) was positive at all initial Cu²⁺ ions concentrations, which showed that the sorption reaction was endothermic, and heat was consumed to transfer the Cu²⁺ ions from aqueous solution onto gyttja. The enthalpy or heat of sorption, ranging from 2.1 to 20.9 kJ mol⁻¹ corresponds a physical sorption, and a range from 20.9 to 418.4 kJ mol⁻¹ indicates a chemical sorption

Table 2 Equilibrium constants and thermodynamic parameters for Cu²⁺ ion sorption onto the gyttja

<i>C_i</i> (mg L ⁻¹)	Temperature (°C)	<i>K_d</i>	ΔG (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)	ΔH (kJ mol ⁻¹)
9.53	25	3.42	-3.03	0.162	45.25
9.53	30	4.41	-3.72		
9.53	35	6.32	-4.72		
19.05	25	1.03	-0.07	0.079	23.44
19.05	30	1.23	-0.52		
19.05	35	1.40	-0.86		
38.10	25	0.65	1.07	0.099	28.88
38.10	30	0.72	0.83		
38.10	35	0.95	0.13		

(Sarı and Tuzen 2008). The ΔH values (23.44–45.25 kJ mol⁻¹) in the present study showed that chemisorption processes predominated for the sorption of Cu²⁺ ions onto the gyttja. Entropy change (ΔS) was also positive (Table 2), and the positive value of the ΔS indicated that the sorption process was probably irreversible and favored complexation and stability of sorption (Donat et al. 2005). These results were in agreement with the results obtained from D–R isotherm.

In order to determine the adsorption kinetics of Cu²⁺ ions onto gyttja, pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental data. The linear form of the pseudo-first order model:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2,303}\right)t \quad (9)$$

where q_e (mg g⁻¹) is the amount of the metal ions on the surface of the sorbent at equilibrium, and q_t (mg g⁻¹) is the amount of the metal ions on the surface of the sorbent at any time, t is time (min), and k_1 (min⁻¹) is the rate constant of the equation. The adsorption rate constants (k_1) can be determined by plotting of $\ln(q_e - q_t)$ versus t . The determination coefficients (R^2 values) for this model ranged from 0.857 to 0.973 at the studied temperatures (Table 3). Ho and McKay (1999) suggested that the pseudo-first-order model fits experimental data well for an initial period of the first reaction step, but this model could not provide the best correlation for chemical sorption process over long periods. Experimental data were also applied to the pseudo-second order kinetic model (Ho 2006):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where k_2 (g mg⁻¹ min⁻¹) is the rate constant of the second-order equation, q_t (mg g⁻¹) the amount of adsorption time t (min) and q_e is the amount of sorption in equilibrium (mg g⁻¹).

The pseudo-second order kinetic model is better correlated with the kinetics data compared with the pseudo-first-order model. The coefficients of determination ($R^2 = 0.999$) were very high for the Cu²⁺ ions sorption onto gyttja, meaning an active sorption processes between Cu²⁺ ions and polar functional groups which can be involved in chemical bonding (Ho 2006). Also, sorption process of divalent metals onto different peat materials were described by the second-order kinetic model (Ho and McKay 1999; Gündoğan et al. 2004). Furthermore, chemisorption processes show a good compliance with the pseudo-second order kinetic model (Ho 2006). This model is more likely to predict the kinetic behavior of sorption with chemical reaction being the rate-controlling step, and it provides best correlation to describe chemical sorption process between the adsorbent and adsorbate (Ho and McKay 1999; Sarı and Tuzen 2008). The data also show that the initial Cu²⁺ ion concentrations influence the sorption capacity, which increased as initial Cu²⁺ ion concentrations increased. These may be attributed to a more efficient utilization of the sorptive capacities of the sorbent because of a higher concentration gradient pressure (Ho and McKay 2000).

The outcomes of the thermodynamic and kinetic experiments showed that the sorption of the Cu²⁺ ions by gyttja was found to be dependent on initial Cu²⁺ ion concentration and temperature. The Freundlich, Langmuir, and D–R isotherms satisfactorily described the sorption data. The value of E calculated using D–R constants was 10.25 kJ mol⁻¹, suggesting that chemical sorption played significant role on the sorption processes. Thermodynamic parameters indicated that sorption process of Cu²⁺ ions by gyttja was spontaneous and endothermic in nature. From the kinetic data, it was found that sorption for Cu²⁺ ions well fitted to the pseudo-second-order kinetic model. As a result, gyttja can be used for the removal of Cu²⁺ from wastewaters and aqueous solutions through a cost-effective and environmentally friendly process. Therefore, it is

Table 3 The pseudo-first order and second-order models parameters for Cu²⁺ ion sorption onto the gyttja at various initial concentrations and temperatures

C_i (mg L ⁻¹)	Temperature (°C)	Pseudo-first order model			Pseudo-second order model		
		q_e (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	q_e (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2
9.53	25	0.271	0.029	0.884	2.23	0.361	0.999
9.53	30	0.252	0.018	0.857	2.26	0.325	0.999
9.53	35	0.282	0.034	0.905	2.36	0.410	0.999
19.05	25	1.209	0.023	0.895	3.90	0.060	0.999
19.05	30	1.126	0.021	0.936	4.00	0.065	0.999
19.05	35	1.073	0.029	0.973	4.10	0.084	0.999
38.10	25	2.187	0.039	0.967	7.02	0.051	0.999
38.10	30	1.695	0.032	0.931	7.16	0.057	0.999
38.10	35	1.456	0.021	0.874	7.59	0.056	0.999

recommended as a suitable, alternatively low-cost sorbent material.

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