

THERMODYNAMIC STUDY OF Cd(II) SORPTION ON SOIL

Raluca-Maria HLIHOR¹, Petronela COZMA¹, Cristina GHINEA¹, Vasile Lucian PAVEL¹,
Brindusa Mihaela ROBU¹, Maria GAVRILESCU¹

¹“Gheorghe Asachi” Technical University of Iași

Abstract

Sorption is a major process responsible for the fate of heavy metals in soils, since the mobility of heavy metals is directly related to their partitioning between the soil solid phase and soil solution. Among the heavy metals cadmium is one of the most toxic with adverse health effects. The objective of this study is to analyze the sorption of Cd(II) from aqueous solution on soil from the industrial area of the city of Iasi (Romania) as a function of temperature at natural pH of the solution using a batch technique. A maximum uptake of about 9.7 mg of cadmium per g of soil and approx. 95 % removal of metal was observed at 20 g/L soil amount, 200 mg/L cadmium solution and 41 °C, with an equilibrium time of 24 hours. Sorption isotherm of Cd(II) on soil were represented by Freundlich and Dubinin-Radushkevich models and the parameters indicated that the sorption of Cd(II) increased with increasing temperature of the system. Enthalpy (ΔH^0), entropy (ΔS^0) and Gibbs free energy (ΔG^0) were calculated from the temperature dependent sorption data, and the results indicated that the sorption of Cd(II) on soil is a spontaneous, feasible and endothermic process.

Key words: heavy metals, isotherms, sorption, temperature

Increase of environmental contamination represents a major consequence of industrial development and a challenge for society. Heavy metal pollution is usually caused by a number of industries such as pigments mining, electroplating, plastics manufacturing, metal plating facilities. Attention has to be paid to the health hazards presented by existence of heavy metals in the environment, because of their accumulation in living tissue through the food chain (Hlihor R.M., Gavrilescu M., 2009; Loukidou M.X. et al., 2004). The problems associated with metal ions discharged in industrial effluents are considerable, due to both their toxic and carcinogenic properties (Ho Y.S. et al., 2002). Cadmium is one of the heavy metals, which is regarded as an element of high toxicity. Originating from metal plating, metallurgical alloying, mining, ceramics and other industrial operations, cadmium proved to be a dangerous pollutant (Sari A. et al., 2003). For the removal of heavy metals from wastewaters physical and chemical processes have been extensively studied. Some of these processes are adsorption, coagulation, flotation, biosorption, chemical precipitation, ultra filtration and electrochemical methods. From this processes, adsorption can be seen as an efficient and economic method to remove the heavy metal pollutants at low concentrations (Kula I. et al., 2006). In order to predict fate and mobility of metal contaminants in soils, an understanding of the sorption process is required because, the

stronger the reaction of metal with soil surface, the less the likelihood environment contamination.

The objectives of this paper are to measure the sorption of Cd (II) from aqueous solution on Iasi area soil as a function of temperature, to achieve sorption thermodynamic data (i.e. ΔG^0 , ΔH^0 , ΔS^0) and to discuss the sorption mechanism.

MATERIAL AND METHOD

Experimental

All chemicals used in this work were of analytical reagent grade and were used without further purification. Cadmium stock solution of 1000 mg/L was prepared by dissolving Cd(NO₃)₂·4H₂O in distilled water. The solution was diluted for different Cd(II) concentrations by deionized water as required working solutions. The concentrations of Cd(II) were analyzed by spectrophotometric method with xylenol orange at 575 nm using a CAMSPEC M-501 UV-VIS spectrophotometer. All the experimental data were the averages of triplicate experiments.

Experiments were carried out using soil samples collected during the summer time from the industrial area of the city of Iasi (Romania), soil that was previously dried at 105 °C in a drying chamber for 3 h and further crushed in a Fritch agate mortar for 30 minutes at a rotative speed of 800 rot/min and separated into different particle size ranges, between 0.25 and above 2 mm. Sorption tests were conducted on a size range of 0.25 – 0.4 mm soil particles.

Equilibrium batch studies were performed at a soil dose of 20 g/L, with a working volume of 25 mL Cd(II) solution of known initial metal concentration (25-200 mg Cd(II)/L) in 150 mL Erlenmeyer flasks at $T = 11-41$ °C. All the experiments were carried-out at the natural pH of the solution (pH=5.5), pH measurements being performed with a HANNA precision pH meter, model pH 213. After 24 h, when the equilibrium was established, the solutions were filtered and the filtrates were analyzed for cadmium concentration.

Metal uptake by soil per mass unit was calculated using the following expression (Eq. 1):

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

where: q is the amount of metal removed from solution (mg/g); C_0 and C_e are the concentration (mg/L) of metal ions in the initial solution and at the equilibrium after the experiment; V (L) is the volume of the solution; m (g) is the amount of soil sample used in the experiment.

Isotherm models

Adsorption isotherm is the basic requirement for designing any adsorption system. Linear regression is frequently used for the determination of the best-fitting isotherm, and the method of least squares has been used for finding the parameters of the isotherms. Experimental data were fitted by Freundlich and Dubinin-Radushkevich isotherm models.

Freundlich isotherm

Freundlich isotherm model stipulate that the ratio of solute adsorbed to the solute concentration is a function of the solution. This model allows for several kinds of sorption sites on the solid and represents properly the sorption data at low and intermediate concentrations on heterogeneous surfaces (Chen L., Gaob X., 2009). can be expressed in linear form by Eq. (2):

$$\log q = \log k_F + \frac{1}{n} \log C_e \quad (2)$$

where k_F ($\text{mg}^{1-n} \text{g}^{-1} \text{L}^n$) represents the sorption capacity when metal ion equilibrium concentration equals to 1; n represents the degree of dependence of sorption with equilibrium concentration.

A plot of $\log(q_e)$ against $\log(C_e)$ gives a straight line graph with $(1/n)$ as the slope and $\log(k_F)$ as the intercept. Both k_F and n determine the curvature and the steepness of the isotherm.

Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich (D–R) isotherm is valid at low concentration ranges and can be used to describe sorption on both homogeneous and heterogeneous surfaces. The D–R isotherm is described by the equation in the linear form (Sari A., Tuzen M., 2008):

$$\ln q = \ln q_{\max} - \beta \varepsilon^2 \quad (3)$$

where q and q_{\max} are defined above, and ε is the Polanyi potential, which is equal to:

$$\varepsilon = RT \ln(1 + 1/C) \quad (4)$$

where R is ideal gas constant (8.3145 J/mol K) and T is the absolute temperature (K).

The saturation limit q_{\max} may represent the total specific micropore volume of the sorbent. The value of β is the activity coefficient related to mean sorption energy (mol^2/kJ^2). It is related with the adsorption mean free energy, E (kJ/mol), defined as the free energy change required to transfer one mole of ions from infinity in solution to the solid surfaces. The relation is as the following:

$$E = \frac{1}{\sqrt{2\beta}} \quad (5)$$

The magnitude of E is useful for estimating the type of sorption reaction. If E is in the range of 8–16 kJ/mol, sorption is governed by chemical ion-exchange. In the case of $E < 8$ kJ/mol, physical forces may affect the biosorption. On the other hand, biosorption may be dominated by particle diffusion if $E > 16$ kJ/mol (Oczan A. et al., 2006).

Thermodynamic studies

Thermodynamic parameters are calculated by using the equation:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

where ΔH^0 , ΔS^0 and T are the enthalpy, entropy, and temperature in Kelvin.

The values of enthalpy (ΔH^0) and entropy (ΔS^0) are obtained from the slope and intercept of $\ln K_d$ vs. $1/T$ plots. The distribution coefficient (K_d) is calculated from the concentration of Cd(II) in suspension (C_0) and that of Cd(II) in supernatant (C_e) after centrifugation according to Eq. (7) (Şeker et al., 2008):

$$K_d = \frac{C_0 - C_e}{C_e} \frac{V}{m} \quad (7)$$

The change of Gibbs free energy (ΔG^0) was calculated from the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

RESULTS AND DISCUSSIONS

Isotherm models

Temperature is one of the most important parameters which dominate metal ions physicochemical behavior in environment (Fan Q. et al., 2009).

Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and the remaining in the solution at a fixed temperature at equilibrium (Ho Y.S. et al., 2002). A maximum uptake of about 9.7 mg/g Cd(II) on soil and aprox. 95 % removal of metal was observed at 20 g/L soil, 200 mg/L cadmium solution and 41 °C, with an equilibrium time of 24 hours (figure not shown).

For the investigation of sorption isotherms, two equilibrium models Freundlich and D-R isotherms were analyzed at different temperatures (11 - 41 °C). The Freundlich isotherm obtained by plotting $\log q_e$ versus $\log C_e$ is shown *fig. 1* and the D-R isotherm is shown in *fig. 2*, in the studied temperature interval.

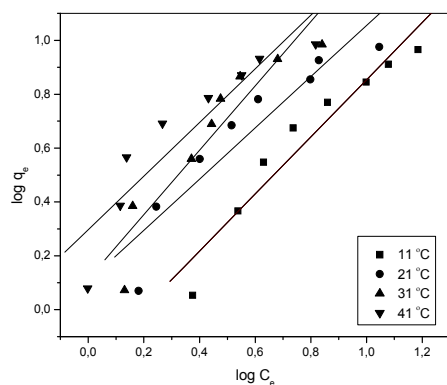


Figure 1 Freundlich isotherm model for Cd(II) sorption on lasi area soil

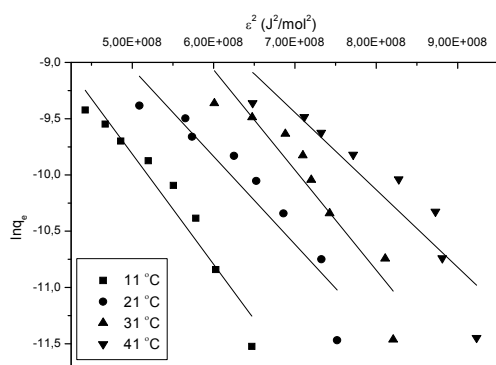


Figure 2 D-R isotherm model for Cd(II) sorption on lasi area soil

The isotherm constants for sorption of Cd(II) on soil at different temperatures are given in Table 1. In the case of Freundlich model, the value of $1/n$ is less than unity, indicating a favorable sorption of Cd(II) on soil. As seen in *fig. 2*, the slopes of D-R plots give the β constant and q_{\max} value, which are calculated from the intercept and slope of the plots. The monolayer sorption capacity is very high ranging from 0.0058 to 0.0242 mol/g for of Cd(II) sorption. The mean sorption energy (E) was calculated as 7.13 kJ/mol for 11 °C, 7.99 kJ/mol for 21 °C and 7.49 kJ/mol for 31 °C indicating the physical nature of Cd(II) sorption on soil. For 41 °C, the value of mean sorption energy (E) was 8.52 kJ/mol, indicating that at higher

temperatures sorption of Cd(II) on soil is governed by chemical ion-exchange. The adsorption pattern of Cd(II) on soil was well fitted by Freundlich isotherm followed by Dubinin-Radushkevich isotherm, according to the values of correlation coefficient, R^2 , higher than 0.9203 for Freundlich model.

Thermodynamic studies

The thermodynamic data calculated by Eqs. 6-8 are listed in Table 2 and were calculated from the slope and intercept of the plot $\ln K_d$ vs. $1/T$ (*fig. 3*). As it can be seen from Table 2 the positive enthalpy change (ΔH^0) in the temperature interval 284.15-313.15 K means that the process of Cd(II) removal from solution is endothermic as expected. The Gibbs free energy change (ΔG^0) is negative for a feasible and spontaneous process under the condition applied. The positive values of entropy (ΔS^0) reflects the affinity of soil particles toward Cd(II) in aqueous solution and may suggest some structural changes on the sorbent (Fan Q. et al., 2009).

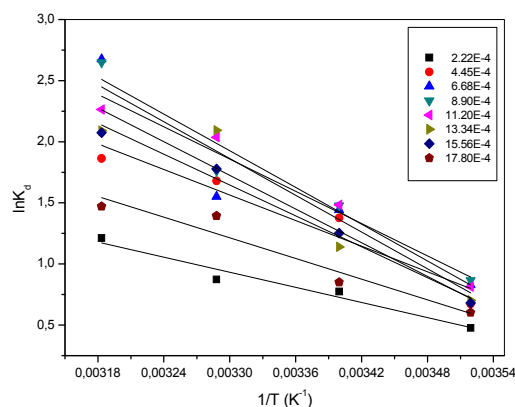


Figure 3 Effect of temperature on the distribution coefficients of Cd(II) on lasi area soil at different initial concentration

CONCLUSIONS

This study focused on the investigation of Cd(II) sorption from aqueous solution on Iasi area soil as a function of temperature at equilibrium using a batch technique.

The experimental results were analyzed by using the Freundlich and Dubinin-Radushkevich isotherm models and the correlation coefficients for fitting the Freundlich equation were significantly better ($R^2 > 0.9203$) than the coefficients for the D-R model. The mean sorption energy (E) was calculated as 7.13-7.99 kJ/mol for the temperature interval 11-31°C, indicating the physical nature of Cd(II) sorption on soil.

Table 1

Sorption isotherm model constants of Cd(II) sorption on lasi area soil

	Temperature (K)	n	K_F (mg/g(L/mg) ^{1/n})	R ²
	Freundlich isotherm	284.15	1.0649	1.608
294.15		1.2461	1.271	0.9338
304.15		1.0009	1.300	0.9336
314.15		1.2129	1.979	0.9203
D-R isotherm		q_{max} (mol/g)	β	R ²
	284.15	0.0074	$9.81 \cdot 10^{-9}$	0.9314
	294.15	0.0058	$7.81 \cdot 10^{-9}$	0.8687
	304.15	0.0242	$8.91 \cdot 10^{-9}$	0.8644
	314.15	0.0097	$6.87 \cdot 10^{-9}$	0.8382

Table 2

The thermodynamic data of Cd(II) sorption on lasi area soil at different Cd(II) initial solution concentrations

C_i (mol/L)	ΔH^0 (kJ/mol)	ΔS^0 (J/molK)	ΔG^0 (kJ/mol)			
			284.15 K	294.15 K	304.15 K	314.15 K
4.45×10^{-4}	29.01	108.73	-1.88	-2.97	-4.06	-5.14
6.68×10^{-4}	41.67	153.01	-1.80	-3.33	-4.86	-6.39
8.90×10^{-4}	41.64	153.43	-2.01	-3.55	-5.08	-6.62
11.20×10^{-4}	36.57	136.14	-2.11	-3.47	-4.83	-6.19
13.34×10^{-4}	38.15	140.24	-1.69	-3.10	-4.50	-5.90
15.56×10^{-4}	34.99	129.15	-1.70	-2.99	-4.29	-5.58
17.80×10^{-4}	23.95	87.41	-0.88	-1.76	-2.63	-3.50

For 41 °C, the value of mean sorption energy (E) was 8.52 kJ/mol, indicating that at higher temperatures sorption of Cd(II) on soil may be governed by chemical ion-exchange. The Gibbs free energy calculated from the thermodynamic data is negative indicating a spontaneous and feasible process. The positive enthalpy value indicated the endothermic nature of the sorption process at studied temperatures. The positive entropy values suggested a increasing in the randomness at the solid/solution interface during the sorption process.

Acknowledgements

This paper was elaborated with the support of BRAIN project *Doctoral scholarships as an investment in intelligence - ID 6681*, financed by the European Social Found and Romanian Government and ID_595 Project within the National Program for Research, Development and Innovation, PN-II.

BIBLIOGRAPHY

- Chen, L., Gaob, X., 2009 - *Thermodynamic study of Th(IV) sorption on attapulgite*, Applied Radiation and Isotopes, vol. 67, p. 1–6.
- Fan, Q., Shao, D., Lu, Y., Wu, W., Wang, X., 2009 - *Effect of pH, ionic strength, temperature and humic substances on the sorption of Ni(II) to Na-attapulgite*, Chemical Engineering Journal, vol. 150, p. 188-195.
- Hlihor, R.M., Gavrilesu, M., 2009 - *Removal of some environmentally relevant heavy metals using low-cost natural sorbents*, Environmental Engineering and Management Journal, vol. 8, p. 353-372.
- Ho, Y.S., Porter, J.F., McKay G., 2002 - *Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, Nickel and Lead single component systems*, Water, Air, and Soil Pollution, vol. 141, p. 1–33.
- Kula, I., Uğurlu, M., Karaoğlu, H., Celik, A., 2008 - *Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by ZnCl₂ activation*, Bioresource Technology, vol. 99, p. 492–501.
- Loukidou, M.X., Karapantsis, T.D., Zouboulis, A.I., Matis, K.A., 2004 - *Diffusion kinetic study of Chromium(VI) biosorption by Aeromonas caviae*, Ind. Eng. Chem. Res., vol. 43, p. 1748-1755.
- Oczan, A., Oncu, E.M., Oczan, A.S., 2006 - *Kinetics, isotherm and thermodynamic studies of adsorption of acid blue 193 from aqueous solutions onto natural sepiolite*, Colloids Surf. A, vol. 277, p. 90-97.
- Sari, A., Mendil, D., Tuzen, M., Soylak, M., 2003 - *Biosorption of Cd(II) and Cr(III) from aqueous solution by moss (Hylocomium splendens) biomass: Equilibrium, kinetic and thermodynamic studies*, Chemical Engineering Journal, vol. 144, p. 1-9.
- Sari, A., Tuzen, M., 2008 - *Biosorption of Pb(II) and Cd(II) from aqueous solution using green alga (Ulva lactuca) biomass*, Journal of Hazardous Materials, vol. 152, p. 302-308.
- Şeker, A., Shahwan, T., Eroğlu, A.E., Yilmaz, S., Demirel, Z., Dalay, M.C., 2008 - *Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II), cadmium(II) and nickel(II) ions on Spirulina platensis*, Journal of Hazardous Materials, vol. 154, p. 973-980.