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APPLICATION OF DIFFERENT ISOTHERM MODELS ON LEAD IONS SORPTION ONTO ELECTRIC FURNACE SLAG

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The effect of temperature on the equilibrium sorption of Pb^{2+} from aqueous solution onto a low-cost electric furnace slag was investigated. In this paper, two-parameter isotherm models namely the Langmuir and the Freundlich and three-parameter isotherm model namely Redlich–Peterson were applied to describe the isotherms and to calculate their constants. The best estimation of the parameters of these models by a non-linear regression analysis was obtained. A comparison between two-parameter and three-parameter isotherms was reported. The characteristic parameters for each isotherms and related coefficient of determination (R^2) have been determined using MATLAB 6.5. All the coefficients of determination (R^2) of the non-linear method are close to unity. The Redlich−Peterson isotherm produced a higher coefficient of determination values in comparison to all the isotherms studied.
Key words: lead, electric furnace slag, sorption isotherm.

Primjena različitih modela izoterma za sorpciju olova na elektropećnoj troski. U radu je ispitan utjecaj temperature na sorpciju Pb^{2+} iona na elektropećnoj troski kao jeftinom sorbensu. Izoterme su opisane uporabom dvo-parametarskih Langmuir i Freundlich modela, te tro-parametarskog Redlich–Peterson modela. Parametri navedenih izotermi određeni su nelinearnom regresijskom analizom. Karakteristični parametri izotermi i koeficijenti određivanja (R^2) određeni su uporabom MATLAB 6.5. Sve vrijednosti koeficijenata određivanja (R^2) su bizu jedan. Najveća vrijednost koeficijenta određivanja (R^2) postignuta je za Redlich−Peterson model.
Ključne riječi: olovo, elektropećna troska, sorpcijska izoterma.

INTRODUCTION

Heavy metals and other metal ions are released into the environment in a number of ways, such as aqueous waste streams of many industries, coal combustion, sewage wastewaters, automobile emissions, battery industry, mining activities, and the utilization of fossil fuels, etc. Heavy metals such as lead, mercury, arsenic, copper, zinc, cadmium are highly toxic when adsorbed into the body [1]. They can cause accumulative poisoning, cancer, brain damage, etc. [2]. Effective methods for metal ions removal that have been used include ion exchange, reverse osmosis, electrochemical treatment, evaporative recovery and adsorption. Cost is an important parameter for comparing the adsorbent materials. Therefore, there is increasing research interest in using alternative low-cost adsorbents. In recent years, considerable attention has been focused on the removal of metal ions from aqueous solution using adsorbents derived

from low-cost materials, such as blast furnace slag [3] and electric furnace slag [4].
Important physicochemical aspect for the evaluation of sorption processes as a unit operation is the sorption equilibrium. Sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that of the interface concentration. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium [5]. The analysis of experimental equilibrium data by fitting into different isotherm models is an important step to propose suitable model for process design. The most widely applied two-parameter isotherms are Freundlich [6] and Langmuir models [7]. Further, other two-parameter models such as Temkin, Dubinin, Jovanovic, Halsey and Hurkins-Jura are also used in the literature [8]. Three-parameter isotherm models namely Redlich–Peterson, Toth, Radke–Prausnitz, Fritz–Schluender, Vieth–Sladek and Sips are also used [9].
Linear or non-linear regression can be used to determine the best fitting isotherm. Non-linear method has been suggested a better way to obtain the equilibrium isotherm parameters, but linear regression is most frequently used to investigate the most fitted isotherm [10].
In this study, a non-linear method of three widely used isotherms, Langmuir, Freundlich, and Redlich-Peterson, were compared in an experiment examining Pb^{2+} ion sorption onto electric furnace slag as low cost sorbent.

EXPERIMENTAL

All sorption experiments were performed on electric furnace slag from the ‘‘Felis’’ foundry in Sisak, Croatia. The chemical composition of electric furnace slag was determined by the standard chemical analysis and results in mass % are: CaO-30 %, MgO-0,2 %, MnO-19 %, SiO_2-19 %, Al_2O_3-1,3 %, FeO-30 %. All experiments have been made with a fraction of particle size of 0.05 to 0.70 mm.
Sorption process of lead onto EFS has been performed by the static, so called “batch” process. The samples of EFS (0.2500 g) have been equilibrated within 8 hours with 50.0 mL of the Pb^{2+} solution of different initial concentration (100, 250, 500, 750 and 1000 mg/L). Experiments were performed at different temperatures (293, 303 and 313 K) and quantity of Pb^{2+} ions remaining in the liquid phase after equilibration has been measured by means of atomic absorption spectrophotometry (AAS, AA-6800, Shimadzu).
The difference between the initial and equilibrium mass concentrations of Pb^{2+} ions is used for calculation of the quantity of lead sorbed on unit mass of electric furnace slag (q, mg Pb^{2+}/g of the EFS), taking into consideration the data related to the EFS weight, volume and mass concentration of the solution. The amount of Pb^{2+} sorbed onto the electric furnace slag was calculated from the following expression:

$$q_e = \frac{(\gamma_0 - \gamma_e) \cdot V}{m} \qquad (1)$$

where q_e is the equilibrium Pb^{2+} concentration sorbed on the electric furnace slag (mg/g), V is the initial volume of the Pb^{2+} solution used (L), m is the mass of electric furnace slag used (g), γ_0 is the initial concentration of Pb^{2+} in the solution (mg/L) and γ_e is the concentration of Pb^{2+} in the solution at equilibrium (mg/L).

RESULTS AND DISCUSSION

The relationship between the amount of Pb^{2+} sorbed and the Pb^{2+} concentration remaining in solution is described by an isotherm. Various isotherm equations can be used to describe the equilibrium characteristics of sorption. The results obtained on the sorption of lead on electric furnace slag were analysed by the well-known models given by Langmuir, Freundlich, and Redlich-Peterson isotherm models.

Langmuir model is the simplest theoretical model for monolayer sorption onto a surface with finite number of identical sites. The Langmuir model [7] is given by the equation:

$$q_e = \frac{q_m K_L \gamma_e}{1 + K_L \gamma_e} \quad (2)$$

where K_L is the sorption equilibrium constant (L/mg).

The Freundlich [6] expression is an empirical equation applicable to non-ideal sorption on heterogeneous surface as well as multilayer sorption, and is expressed by the following equation:

$$q_e = K_F \cdot \gamma_e^{1/n} \quad (3)$$

where K_F ((mg/g)(L/mg)$^{1/n}$)) and n are the Freundlich constants related to the sorption capacity and sorption intensity, respectively. The Freundlich exponent, n, should have values in the range of 1 to 10 for classification as favourable adsorption.

Redlich and Peterson (1959) incorporated three parameters into an empirical isotherm. The Redlich-Peterson isotherm model combines elements from both the Langmuir and Freundlich equations, and the mechanism of adsorption is a hybrid unique and does not follow ideal monolayer adsorption [11]. It can be described as follows:

$$q_e = \frac{K_R \gamma_e}{1 + a_R \gamma_e^{\beta}} \quad (4)$$

Where q_e (mg/g) is the solid-phase sorbate concentration at equilibrium, γ_e (mg/L) is the concentration of adsorbate in equilibrium with liquid phase, K_R (L/g) and a_R (L/mol) are the Redlich-Peterson isotherm constants, while β is the exponent, which lies between 0 and 1. When exponent β =0, Eq. (4) transforms to Henry`s law equation. For exponent β = 1, Eq. (4) converts to the Langmuir form.

In order to asses different isotherms and their ability to correlate with experimental results, the theoretical plots from each isotherm have been fitted with the experimental data for sorption of Pb^{2+} ions on electric furnace slag. The experimental data of the amount Pb^{2+} sorbed onto the EFS at different temperatures were fitted to the isotherm models using MATLAB 6.5 and the graphical representations of these models are presented in Figures 1A, 1B and 1C. All isotherm parameters obtained using the non-linear method for the sorption of Pb^{2+} ions onto electric furnace slag at different temperatures were presented in Table 1. All the coefficients of determination (R^2) of the non-linear method are close to unity. The experimental data yielded excellent fits within the following isotherms order: Redlich−Peterson > Langmuir > Freundlich, based on its R^2 values.

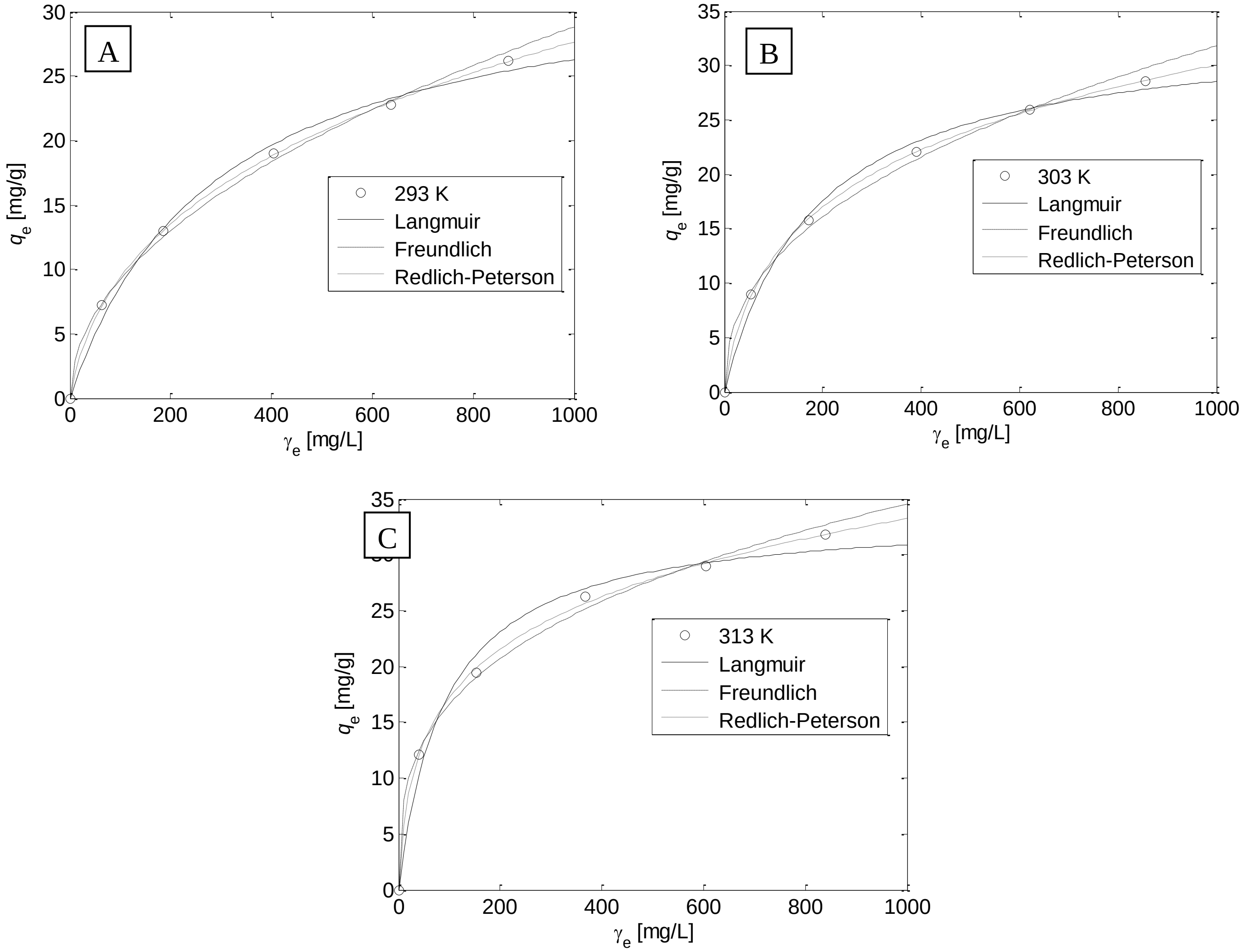

Figure 1. Experimental data (points) and the non-linear sorption isotherm models (lines) for Pb^{2+} with EFS at: (A) T = 293 K, (B) T = 303 K and (C) 313 K.

Slika 1. Eksperimentalni podatci (točke) i modeli nelinearne sorpcije (linije) Pb^{2+} iona na elektropećnoj troski pri: (A) T = 293 K, (B) T = 303 K i (C) 313 K.

Table 1. Isotherm parameters obtained using the non-linear method for the sorption of Pb^{2+} ions onto electeric furnance slag at different temperatures.
Tablica 1. Parametri izotermi dobiveni nelinearnom metodom za sorpciju Pb^{2+} iona na elektropećnoj troski pri različitim temperaturama.

		Temperature (K)		
Isotherm	**Parameter**	**293**	**303**	**313**
Freundlich	n	2.02429	2.36742	3.14465
	K_F ((mg/g)(L/mg)$^{1/n}$))	0.9502	1.7182	3.8405
	R^2	0.9964	0.9927	0.9937
Langmuir	q_m (mg/g)	33.93942	33.79055	33.72579
	K_L (L/mg)	0.00342	0.00543	0.01089
	R^2	0.99471	0.99481	0.98734
Redlich-Peterson	β	0.66975	0.75965	0.77675
	a_R (L/mol)	0.26772	0.36042	1.08027
	K_R (L/g)	0.08501	0.05784	0.14729
	R^2	0.99990	0.99996	0.99905

CONCLUSIONS

The present investigation shows that the electric furnace slag is an effective adsorbent for the removal of Pb^{2+} ions from aqueous solutions. The sorption of Pb^{2+} on the electric furnace slag was found to be initial concentration and it is physical sorption. The amount of Pb^{2+} removed increases with the increase temperature and initial Pb^{2+} concentration. The equilibrium data have been analyzed using Langmuir, Freundlich and Redlich-Peterson isotherms.

The characteristic parameters for each isotherm and related coefficients of determination (R^2) have been determined using MATLAB 6.5. The experimental data yielded excellent fits within the following isotherms order Redlich−Peterson > Langmuir > Freundlich, based on their coefficient of determination (R^2) values. The Redlich−Peterson isotherm produced a higher coefficient of determination values (0.99990, 0.99996 and 0.99905 for experiments performed at 293, 303 and 313 K, respectively) in comparison to all the isotherms studied.

REFERENCES

1. L. Ćurković, Š. Cerjan-Stefanović, T. Filipan, Water Research, 31, 1997, 1379-1382.
2. J. Perić, M. Trgo, N. Vukojević Medvidović N, Water Research, 38, 2004, 1893-1899.
3. S.V. Dmitrova, Wat. Res., 30, 1996, 228–232.
4. L. Ćurković, Š. Cerjan-Stefanovic, A. Rastovčan-Mioč, Water Research, 35, 2001, 3436-3440.
5. Y.S. Ho, A.E. Ofomaja, Process Biochemistry, 40, 2005, 3455–3461.
6. H.Z. Freundlich, The Journal of Physical Chemistry, 57A, 1906, 385-470.
7. I. Langmuir, Journal of the American Chemical Society, 40, 1918, 1361-403.
8. M. R. Samarghandi, M. Hadi, S. Moayedi, F. Barjasteh Askari, Iranian Journal of Environmental Health Science and Engineering, 6, 2009, 4, 285-294.
9. K. Vasanth Kumar, K. Porkodi, Journal of Hazardous Materials, 138, 2006, 3, 633-635.
10. Y.S. Ho, Polish Journal of Environmental Studies 15, 2006, 1, 81–86.
11. O. Redlich, D.L. Peterson, The Journal of Physical Chemistry, 63, 1959, 1024-1026.