Mathematical Prediction of Sorption Processes of Heavy Metals on Cation Exchangers Using the Thomas Model

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ABSTRACT

On a production scale, it is advisable to use mathematical models for predicting the treatment of effluents from heavy metal ions, which will increase the efficiency of enterprises. The sorption processes of copper, zinc, nickel and cadmium ions on the KU-2-8 cation exchange resin in the acid form at different concentrations were studied in this scientific work. At the same time, the sorption curves calculated were constructed using the Thomas model. The study results showed that this model very clearly describes the sorption processes of metals on the resin. Thus, it can be used to predict the processes of wastewater treatment in production.

Keywords: heavy metals, ion exchange, sorption, Thomas model, wastewater treatment.

INTRODUCTION

The level of heavy metal pollution has risen sharply over the past 50 years as a result of the exponential increase in the use of heavy metals in industrial processes. They formed in the process of human life and have become one of the most dangerous hydrosphere pollutants [Mushtaq et al. 2020; Jaiswal et al. 2018]. The metals that infiltrate into water bodies can concentrate in organisms and form toxic compounds while migrating in the ecosystem along food chains [Pawan 2012; Li et al. 2020; Zhou et al. 2020].

Heavy metals in the periodic table of elements are one of the large groups with an atomic mass of more than 50 atomic units. This group includes more than 40 metals, such as copper, zinc, cadmium, lead, chromium, nickel, cobalt, iron and others [Chen 2012; Mance 1987].

The sources of metals entering the aquatic environment are non-ferrous metallurgy, paint and varnish industry, machine-building industry, galvanic production, production of batteries [Sonone et al. 2020; Dolina 2008]. The chemical composition and concentration of effluents of these industries are pretty diverse in quantitative and qualitative characteristics, including, for example, such areas as chromium plating, copper plating, galvanizing etc. Urban wastewater treatment plants are sometimes insufficient to treat such wastewater, so they should be treated directly at enterprises, introducing technologies into production processes. Physicochemical, chemical and biological methods can carry out wastewater treatment from heavy metal ions. One of the promising methods is ion exchange. Its advantages are: cleaning to the water quality criteria, reusing water after purification, treating mixed effluents, selective releasing substances from water, reusing ion exchange resins after their regeneration.

In order to predict the efficiency of wastewater treatment from metal ions on an industrial scale, mathematical models, such as Langmuir, Henry isotherms, Thomas, Friendlich models, etc., are used increasingly often.

For the mathematical description of the initial sorption curves under dynamic conditions (dependence between the concentration of ions in the eluate and the sorption time (or the missed volume of the solution)) at a given constant filtration rate of the solution through a column with cation exchange resin, the Thomas model [Thomas 1944; Hanbali et

al. 2014; Xu et al. 2013; Nwabanne et al. 2012] is used most often. It is one of the most reliable models, characterized by simplicity, ease of use and it well describes the physico-chemical processes.

MATERIAL AND METHODS

Model solutions of metal sulfates: copper, zinc, cadmium and nickel were used to study the sorption processes. The metal concentrations were 10 meq/dm^3, 20 meq/dm^3 and 50 meq/dm^3. The ion exchanger with a volume of 20 cm^3 was placed in a glass column with a diameter of 2 cm [Koliehova et al. 2019]. The solution consumption of the sorption process ranged from 10 cm^3/min to 15 cm^3/min. In the sorption process, the samples with a volume of 100 cm^3 to 500 cm^3 were taken. The model solution with metal was passed through the ion exchange column filled with a cation exchange resin KU-2-8. The concentration of heavy metal ions, acidity, alkalinity and pH were monitored in the selected samples.

TEDC (the total exchange dynamic capacitance) of the metals sorbed on the cation exchange resin was determined by the formula, meq/dm^3:

$$TEDC = \sum_{i=1}^{n} \frac{(C_{init.} - C_i) \cdot V_s}{V_i} \qquad (1)$$

where: $C_{init.}$ is the initial metal ions concentration in the solution, meq/dm^3; V_i is the volume of cationite, cm^3; C_i is the metal ions concentration in the i-th sample, meq/dm^3; V_s is the volume of sample, cm^3; n is the number of samples taken.

The Thomas model was used for mathematical modeling of sorption processes. Thomas model is described by the dependence:

$$\frac{C}{C_0} = \frac{1}{1 + exp\left(K\left(\frac{QM}{v} - C_0 t\right)\right)} \qquad (2)$$

where: K is the constant of the Thomas model, dm^3/mg·h; Q is the maximum metal concentration in the solid phase, mg/g; v is the volumetric rate of solution filtration through the column (the solution consumption through the column), dm^3/h; M is the sorbent mass, g; t is time, h; C is the metal concentration in the solution, meq/dm^3; C_0 is the initial metal concentration, meq/dm^3.

The filtration time was calculated when measuring the volumes of filtered solutions and a constant filtration rate by the formula:

$$t = \frac{V_p}{v} \qquad (3)$$

where: V_p is the volume of the filtered solution.

The application of the Thomas model, which describes the dynamic sorption curves, is reduced to determining the constant of the Thomas model (Table 1) by experimental results. The kinetic coefficient and the sorption column capacity can be determined by the linear dependence of $ln(C/C_0-1)$ on 1 (or V_p/v). The dependence can be represented as:

$$ln\left(\frac{C_0}{C} - 1\right) = K\left[\frac{QM}{v} - C_0\left(\frac{V_p}{v}\right)\right] \qquad (4)$$

$$K = \frac{ln(\frac{C_0}{C} - 1)}{[\frac{QM}{v} - C_0\left(\frac{V_p}{v}\right)]} \qquad (5)$$

The mass was calculated for 20 cm^3 of the cation exchange resin KU-2-8 based on the specific volume of 2.7 cm^3/g: M = 7.4 g. In the case of the sorption of copper ions under dynamic conditions, the kinetic coefficient (the constant of the Thomas model) was equal to 0.00976 dm^3/mg·h (Table 1). The maximum concentration of the metal at the selected concentrations of C_0 was determined by TDEC:

$$Q = E_t \frac{V_i N}{1000 \cdot M} \qquad (6)$$

where: E_t is TEDC, meq/dm^3; N is the equivalent metal weight, for Cu^{2+} 31.77 mg; M is the resin mass, g (for this case 7.4 g); V_i is the resin volume, cm^3.

For example, based on equation (2) for copper ions, the Thomas model can be written as:

$$C = \frac{C_0}{1 + exp[0.00976(\frac{QM}{v} - C_0\left(\frac{V_p}{v}\right)]} \qquad (7)$$

RESULTS AND DISCUSSION

Figures 1–3 show the initial sorption curves of copper, zinc, nickel and cadmium ions on the KU-2-8 cation exchange resin at initial metal concentrations of 10 meq/dm^3, 20 meq/dm^3 and

Table 1. The value of the constant K for the Thomas model of the initial curves of sorption of copper, zinc, cadmium and nickel on the cation exchange resin KU-2-8

Form of cation exchange resin	Metal			
	Cu	Zn	Cd	Ni
H^+	0.00976	0.0130	0.0050	0.01218

50 meq/dm³. The choice of these concentrations was due to the fact that with a cation exchange resin capacity of approximately 2000 meq/dm³, even with the cation exchange resin volume of 20 cm³, the volume of solutions filtered through the cation exchange resin reaches 1–6 dm³. The time to construct each curve will be quite significant at the solution consumption of 0.9 dm³ per hour at selected concentrations. If the heavy metal concentrations are 1–2 orders of magnitude lower, the research time will stretch for months and years. On the other hand, the mathematical processing of the results will allow predicting the efficiency of the resin and the extraction of heavy metal ions at much lower concentrations.

As shown in Figure 1, the total exchange dynamic capacity (TEDC) of the cation exchange resin in the H +-form on the metal cations reached approximately 2000 meq/dm³. The capacity to breakdown reached approximately 1000 meq/dm³. The solution's initial concentration of copper, zinc, nickel, and cadmium reached 10 meq/dm³.

The TEDC of cation exchange resin reached approximately 2100 meq/dm³ and the dynamic exchange capacity before breakdown was 1100 meq/dm³ at the metal concentration of 20 meq/dm³ (Figure 2). The TEDC of cation exchange resin amounted to 2090 meq/dm³ and the dynamic exchange capacity before breakdown – 1050 meq/dm³ at the initial concentration of metals 50 meq/dm³ (Figure 3).

In this case, the ion exchange processes took place in equivalent quantities and the extraction efficiency of heavy metal ions in the selected ranges of initial concentrations varied little. The main indicators – the TEDC of the cation exchange resin and the exchange dynamic capacity before breakdown (EDC_b) that does not depend on the initial concentration. The breakdown concentration, in this case, was taken as the concentration of metals 1 mg/dm³.

The ion exchange equivalence was also indicated by the data on the change in the acidity of solutions during the sorption of metal ions (Figs. 1–3). In general, the initial solution acidity when passing through the cation exchange resin in the acid form is proportional to the amount of sorbed metals, regardless of the initial concentration of metal ions. The higher the initial concentration of the solution of copper, zinc, nickel and cadmium ions, the higher the acidity of the filtered solution, the lower the pH of these solutions. At the concentration of heavy metal sulfate of 10 meq/dm³ (Fig. 1), the acidity varied in the range of 10–0.1 meq/dm³, and the pH increased from 2.22 to 4.08. At the concentration of metal solutions of 20 meq/dm³ (Fig. 2), the acidity varied from 20 meq/dm³ to 0.01 meq/dm³, and the pH increased from 1.60 to 4.55; at 50 meq/dm³ (Fig. 3), the acidity
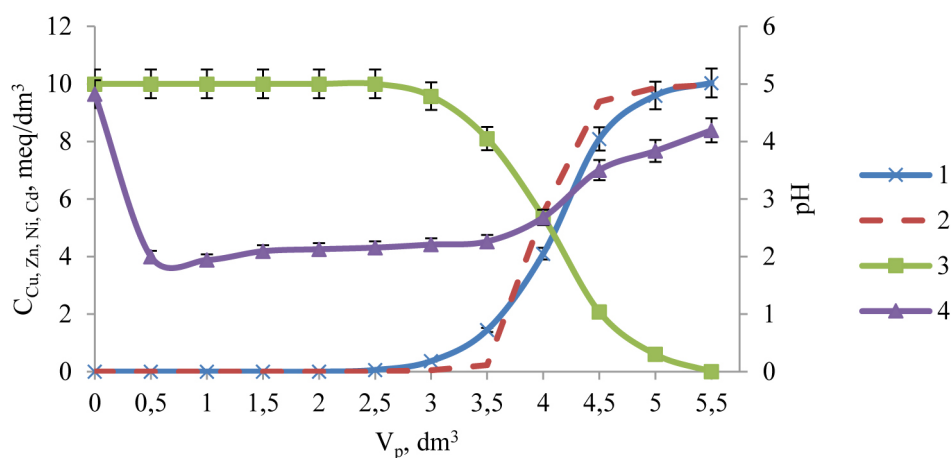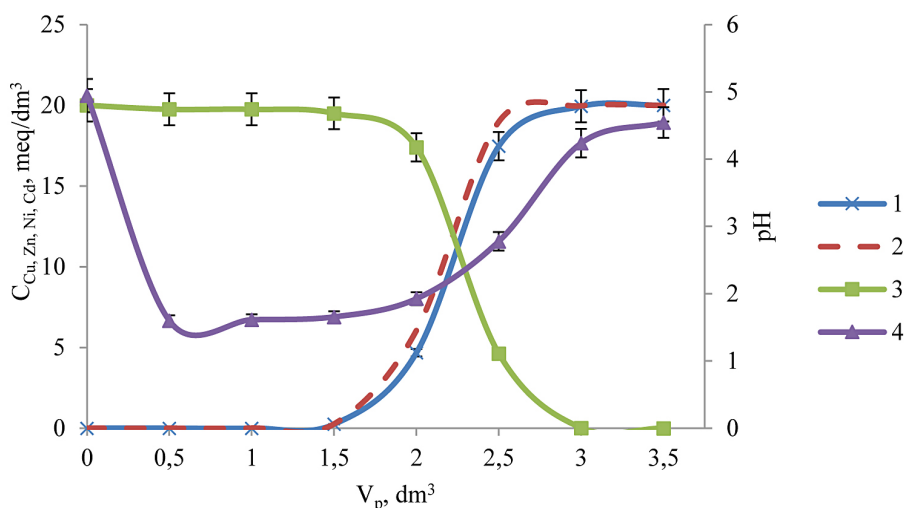

Figure 1. The average values of the concentration of copper, zinc, nickel and cadmium (1), acidity (3), pH (4) from the volume of 0.01 n solutions of metal sulfates passed through the cation exchange resin KU-2-8 in the H^+ - form (V_i = 20 cm³). Curve (2) was calculated according to the Thomas model

Figure 2. The average values of the concentration of copper, zinc, nickel and cadmium (1), acidity (3), pH (4) from the volume of 0.02 n solutions of metal sulfates passed through the cation exchange resin KU-2-8 in the H$^+$ - form (V_i = 20 cm^3). Curve (2) was calculated according to the Thomas model
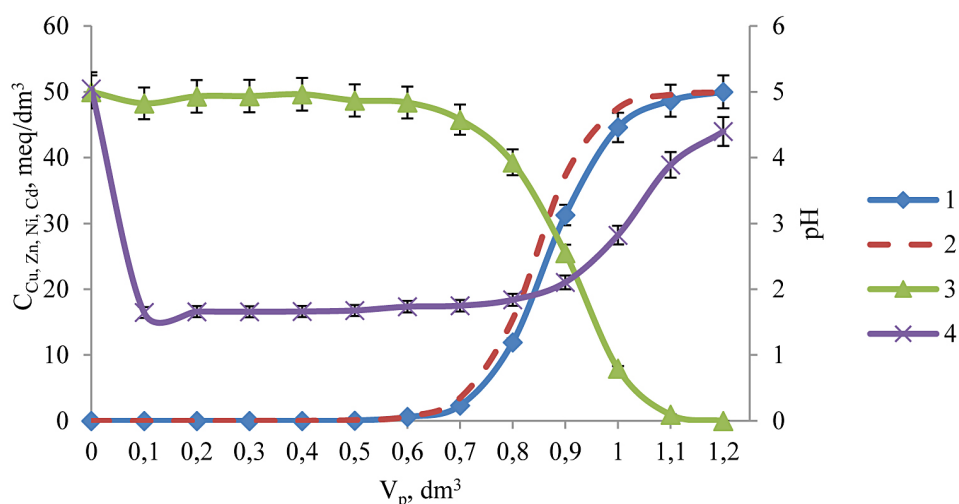

Figure 3. The average values of the concentration of copper, zinc, nickel and cadmium (1), acidity (3), pH (4) from the volume of 0.05 n solutions of metal sulfates passed through the cation exchange resin KU-2-8 in the H$^+$ - form (V_i = 20 cm^3). Curve (2) was calculated according to the Thomas model

decreased from 50 meq/dm^3 to 0.05 meq/dm^3, the pH increased from 1.57 to 4.5.

The theoretically obtained curves of the Thomas model (Fig. 1–3) coincide with the experimental curves of the sorption of heavy metals.

CONCLUSIONS

The sorption processes of copper, zinc, cadmium and nickel ions on the KU-2-8 cation exchange resin in the acid form at different concentrations of heavy metals were studied.

The mathematical Thomas model for the initial sorption curves of metals on the cation

exchange resin KU-2–8 in the H$^+$ -form under dynamic conditions at the constant filtration rate of the solution through the column was calculated. The theoretically calculated curves coincide with the curves obtained experimentally in approximately 95%. This mathematical model can be used to predict the efficiency of wastewater treatment from heavy metal ions.

REFERENCES

1. Chen J.P. 2012. Decontamination of Heavy Metals: Processes, Mechanisms, and Applications. CRC Press/Taylor and Francis Group, USA.

2. Dolina L.F. 2008. Sovremennaya tekhnika i tekhnologii dlya ochistki stochnykh vod ot soley tyazhelykh metallov: monografiya. Kontinent, Dnepropetrovsk. (in Russian)

3. Hanbali M., Holail H., Hammud H. 2014. Remediation of lead by pretreated red algae: adsorption isotherm, kinetic, column modeling and simulation studies. Green Chemistry Letters and Reviews, 7(4), 342–358. DOI: 10.1080/17518253.2014.955062.

4. Jaiswal A., Verma A., Jaiswal P. 2018. Detrimental Effects of Heavy Metals in Soil, Plants, and Aquatic Ecosystems and in Humans. J Environ Pathol Toxicol Oncol., 37(3), 183–197. DOI: 10.1615/JEnvironPatholToxicolOncol.2018025348.

5. Koliehova A., Trokhymenko H., Melnychuk S., Gomelya M. 2019. Treatment of Wastewater Containing a Mixture of Heavy Metal Ions (Copper-Zinc, Copper-Nickel) using Ion-Exchange Methods. Journal of Ecological Engineering, 20(11), 146–151. DOI: 10.12911/22998993/112746

6. Li R., Tang X., Guo W., Lin L., Zhao L., Hu Y., Liu M. 2020. Spatiotemporal distribution dynamics of heavy metals in water, sediment, and zoobenthos in mainstream sections of the middle and lower Changjiang River. Science of The Total Environment, 714, 136779. DOI: 10.1016/j.scitotenv.2020.136779.

7. Mance G. 1987. Pollution threat of heavy metals in aquatic environments. Springer Netherlands, England.

8. Mushtaq N., Singh D.V., Bhat R.A., Dervash M.A., Hameed O. 2020. Freshwater Contamination: Sources and Hazards to Aquatic Biota. Fresh Water Pollution Dynamics and Remediation. Springer, Singapore. DOI: 10.1007/978-981-13-8277-2_3

9. Nwabanne J., Igbokwe P. 2012. Kinetic Modeling of Heavy Metals Adsorption on fixed bed Column. International Journal of Environmental Research, 6(4), 945–952. DOI: 10.22059/ijer.2012.565.

10. Pawan K.B. 2012. Heavy Metals in Environment. Lambert Academic Publishing, Germany.

11. Sonone S., Jadhav S., Singh Sankhla M., Kumar R. 2020. Water Contamination by Heavy Metals and their Toxic Effect on Aquaculture and Human Health through Food Chain. Letters in Applied NanoBioScience, 10, 2148–2166. DOI: 10.33263/LIANBS102.21482166.

12. Thomas H.C. 1944. Heterogeneous Ion Exchange in a Flowing System. J. Am. Chem. Soc., 66, 1664–1666. DOI: 10.1021/ja01238a017.

13. Xu Z., Cai J., Pan B. 2013. Mathematically modeling fixed-bed adsorption in aqueous systems. J. Zhejiang Univ. Sci. A., 14, 155–176. doi:10.1631/jzus.A1300029.

14. Zhou Q., Yang N., Li Y., Ren B., Ding X., Bian H., Yao X. 2020. Total concentrations and sources of heavy metal pollution in global river and lake water bodies from 1972 to 2017. Global Ecology and Conservation, 22, e00925. DOI: 10.1016/j.gecco.2020.e00925.