Scientific Papers. Series E. Land Reclamation, Earth Observation & Surveying, Environmental Engineering. Vol. III, 2014
Print ISSN 2285-6064, CD-ROM ISSN 2285-6072, ISSN-L 2285-6064

COPPER REMOVAL: KINETIC AND THERMODYNAMIC STUDY

Gabriela BUEMA[1], Sorin Mihai CIMPEANU[2], Daniel Mircea SUTIMAN[1], Razvan TEODORESCU[2], Daniela BURGHILA[2], Ramona Carla CIOCINTA[3], Daniel BUCUR[3], Maria HARJA[1*]

[1] "Gh. Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Prof. dr. doc. D. Mangeron Street no. 73, 700050, Iasi, Romania
E-mail: buema_gabrielaa@yahoo.com; maria_harja06@yahoo.com; daniel_sutiman@yahoo.com
[2] University of Agronomic Sciences and Veterinary Medicine of Bucharest, 59 Marasti Blvd., 011464, Bucharest, Romania, mscimpeanu@yahoo.fr, razvan.iteodorescu@gmail.com
[3] "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine of Iasi, Faculty of Agriculture, 3, Mihail Sadoveanu Alley, 700490, Iasi, Romania, dbucur@uaiasi.ro

Abstract

The capacity of one material synthesized from ash to remove Cu^{2+} from aqueous solutions was evaluated. Adsorption kinetics measurements were performed at 298, 308 and 323 K and thermodynamic parameter was calculated. The adsorption process was found to be feasible and spontaneous due to negative value of Gibbs free energy (−6.91 kJ mol^{-1} at 25 °C). Kinetic studies have been carried out to evaluate Cu^{2+} adsorption using a number of three parametric equations: the pseudo first order, pseudo second order and intra-particle diffusion model equations. Results obtained showed that for all the studied temperatures the adsorption process follows a pseudo second order kinetic model, which demonstrates that the chemical adsorption process is predominantly.

Key words: adsorption, copper ions, kinetic, low cost adsorbent, thermodynamic

INTRODUCTION

Heavy metals pollution in the aqueous system is still a worldwide concern due to their detrimental effects to human health and living ecosystem (Idris et al., 2012; Doskočil and Pekař, 2012; Javadian et al., 2013; Buema et al., 2014). Copper ion is the most commonly metal found in contaminated waters. This toxic metal ion is being introduced into natural water system from various industrial activities. The only health-based guideline value for copper proposed by the World Health Organization is 2 mg Cu L^{-1}. The common treatment processes for wastewater treatment can be physical, chemical and biological. From these methods, adsorption proved to be the most accepted treatment method to eliminate diverse types of heavy metals from wastewaters. In present modified ashes obtained by different methods were frequently used as adsorbents for wastewater treatment. However, the specialized literature recommends the use of modified ash for removal of heavy metals due to its higher capacity uptake (Harja et al., 2012; Harja et al., 2013; Kouamo Tchakoute et al., 2013; Shoumkova and Stoyanova, 2013; Sommerville et al., 2013; Vereshchagina et al., 2013; Zhang et al., 2013).

In this study, the modified ash obtained by alkaline treatment was used as low-cost adsorbents for the removal of copper ions from aqueous solution. The ability of this material in the copper ions removing was studied by batch technique. The kinetics data were modeled using three kinetics models: pseudo-first order, pseudo-second order and intra-particle diffusion models, in order to understand the adsorption mechanism of copper ions onto considered low-cost adsorbents.

MATERIALS AND METHODS

Methods of analysis

The material used for this work was selected based on previous studies. The modified material was characterized by different techniques such as: SEM–EDS, BET surface area, FT-IR and XRD. The chemical and the mineralogical characterizations results are presented in the literature (Harja et al., 2012;

Scientific Papers. Series E. Land Reclamation, Earth Observation & Surveying, Environmental Engineering. Vol. III, 2014
Print ISSN 2285-6064, CD-ROM ISSN 2285-6072, ISSN-L 2285-6064

Harja et al., 2013; Curteanu et al., 2014; Buema et al., 2014).

The adsorption experiments

Adsorption study was determined using the batch equilibrium method. An original solution of Cu(II) ions was prepared by dissolving 1.9661 g of accurately weighed $CuS0_4 \cdot 5H_20$ in 1 L distilled water to give a Cu(II) ions concentration of 500 mg L^{-1}. The pH of Cu(II) solutions was adjusted to 5 with HCl. At certain time intervals, the samples were collected and filtered. The concentration of Cu(II) ions was measured by spectrophotometrically and calculated from absorbance in the visible spectrophotometer. The adsorption of Cu(II) was studied after adding 2 g of adsorbent into 200 mL of aqueous solution containing Cu(II) and shaking at 300 rpm for 2 hours at 298, 308 and 323K.

The adsorption uptake was calculated by following relation:

$$q = \frac{(C_0 - C)}{m_s} V$$

where q is the uptake (mg g^{-1}), C_0 and C are the liquid phase concentration of copper at initial and equilibrium (mg L^{-1}), V is the volume (L) and m_s is the amount of adsorbent (g).

RESULTS AND DISCUSSIONS

Effect of temperature on the adsorption

Fig. 1 shows the effect of temperature on the adsorption of Cu(II).

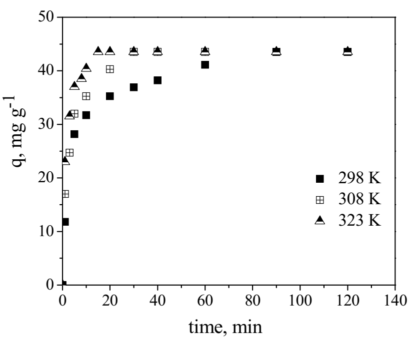

Figure 1. Effect of temperature on adsorption

The equilibrium adsorption capacity of Cu(II) is 43.53 mg g^{-1} at 298, 308 and 323 K, respectively, obtained after 90, 30 and 15 minutes, indicating that the adsorption of Cu(II) on adsorbent is endothermic (Sheng et al., 2010; Hashemian and Mirshamsi, 2012).

Adsorption kinetics analysis

In table 1 are presented the kinetic parameters obtained from the graphs by plotting $log(q_e - q)$ against t, t/q against t, q against $t^{1/2}$, respectively.

Table 1. Kinetic parameters

T,K	Pseudo first model	Pseudo second model	Intra-particle diffusion
298	$R^2 = 0.889$	$R^2 = 0.997$ $q_e = 43.53$ $k_2 = 0.0063$	$R^2 = 0.766$
308	$R^2 = 0.926$	$R^2 = 0.997$ $q_e = 43.53$ $k_2 = 0.0165$	$R^2 = 0.667$
323	$R^2 = 0.928$	$R^2 = 0.997$ $q_e = 43.53$ $k_2 = 0.0406$	$R^2 = 0.471$

In the case of pseudo second order model, the values of correlation coefficients, R^2, are found to be all extremely high ($R^2 = 0.997$) for all the temperatures which further indicates that the mechanism concerning adsorption of Cu(II) can be explained by pseudo-second-order reaction kinetic model (Table 1).

In the figure 2 is presented plots of the pseudo-second order kinetics.

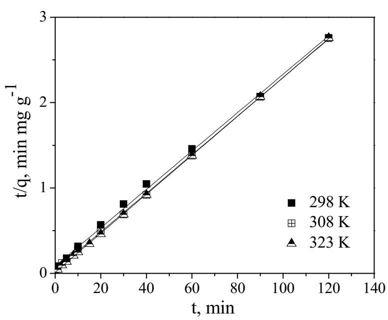

Figure 2. Plots of the pseudo-second order kinetics

Besides, increasing the temperature leads to an increase in the value of k_2 shows that the adsorption of is endothermic and increasing temperature favors the adsorption, which is the same with the result described above.

Also, it was calculated the initial adsorption rate, h, as t → 0 by:

$$h = k_2 q_{eq}^2$$

The values obtained for the adsorbent were: 11.94 mg/g min, 31.26 mg/g min and 76.93 mg/g min at 298 K, 308 K and 323 K.

Adsorption thermodynamic analysis

The Gibbs free energy (ΔG^0) and the activation energy (E_α) for Cu(II)-adsorption onto adsorbent were calculated on the basis of the experimental data.

The Gibbs free energy (ΔG^0) was calculated using the following equation:

$$\Delta G^0 = -RT lnK$$

where R is the universal gas constant (8.314 J/mol K), T is the temperature (K), and the K value was obtained by Langmuir equation.

The ΔG^0 values obtained was −6.91 kJ mol^{-1} at 25^0C.

The values of lnk_2 versus 1/T are plotted and shown in Fig. 3. There is a good linear relationship with the values of slope and intercept proved by the correlation coefficient R^2 - *0.978.*

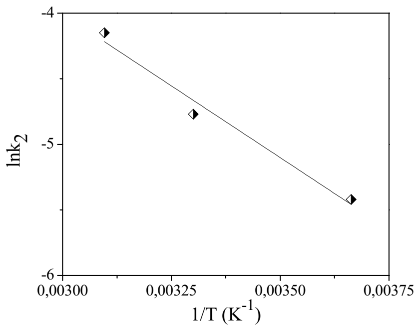

Figure 3. A plot against lnk_2 to 1/T for removal of Cu(II)

The E_α value obtained was 16.62 kJ mol^{-1}. This result is well above the characteristic range for the physisorption (5-20 kJ mol^{-1}), fact that could be taken as indication of the complexity of the overall uptake process (Ho et al., 2001).

CONCLUSIONS

Adsorption kinetics measurements were performed at 298, 308 and 323 K and thermodynamic parameter was calculated.

Copper ion adsorption is dependent on temperature, with the increase of this parameter, the maximum capacity being achieved after 90, 30 and 15 minutes at 298, 308 and 323 K.

The adsorption process can be described well by pseudo-second-order kinetic model.

The adsorption process was found to be feasible and spontaneous due to negative value of Gibbs free energy (−6.91 kJ mol^{-1} at 25^0C).

The study of thermodynamic parameters have shown the feasibility and spontaneous adsorption process of Cu^{2+} onto the material obtained by treating ash with the solution of NaOH (solid/liquid ratio 1:5) for 4 h at 90^0C.

The experimental results presented in this study shown that this material can be an efficient alternative for the removal of copper ions from wastewater at different temperatures, because is available in large quantities and is simply to obtain.

REFERENCES

Buema G., Misaelides P., Noli F., Sutiman D.M., Cretescu I., Harja M., 2014. Uranium removal from aqueous solutions by raw- and modified power plant ash. Journal of Radioanalytical and Nuclear Chemistry, 299, 381–386.

Curteanu S., Buema G., Piuleac C.G., Sutiman D.M., Harja M., 2014. Neuro-evolutionary optimization methodology applied to the synthesis process of ash based adsorbents. Journal of Industrial and Engineering Chemistry , 20, 597-604.

Doskočil L., Pekař M., 2012. Removal of metal ions from multi-component mixture using natural lignite. Fuel Processing Technology, 101, 29–34.

El Haddad M., Mamouni R., Saffaj N., Lazar S., 2012. Removal of a cationic dye – Basic Red 12 – from aqueous solution by adsorption onto animal bone meal Journal of the Association of Arab Universities for Basic and Applied Sciences, 12, 48–54.

El Haddad M., Slimani R., Mamouni R., Laamari R., Rafqah S., Lazar S., 2013. Evaluation of potential capability of calcined bones on the biosorption removal efficiency of safranin as cationic dye from aqueous solutions. Journal of the Taiwan Institute of Chemical Engineers, 44, 13–18.

Harja M., Buema G., Sutiman D. M., Munteanu C., Bucur D., 2012. Low cost adsorbents obtained from ash for copper removal. Korean Journal of Chemical Engineering, 29, 1735-1744.

Harja M., Buema G., Sutiman D. M., Cretescu I., 2013. Removal of heavy metal ions from aqueous solutions using low-cost sorbents obtained from ash. Chemical Papers, 67, 497–508.

Hashemian S., Mirshamsi M., 2012. Kinetic and thermodynamic of adsorption of 2-picoline by sawdust from aqueous solution. Journal of Industrial and Engineering Chemistry, 18, 2010–2015.

Ho Y.S., Ng J.C.Y., McKay G., 2001. Removal of lead (II) from effluents by sorption on peat using second-order kinetics, Separation Science and Technology, 36, 241–26**.**

Idris A., Ismail N.S.M., Hassan N., Misran E., Ngomsik A.F., 2012. Synthesis of magnetic alginate beads based on maghemite nanoparticles for Pb (II) removal in aqueous solution. Journal of Industrial and Engineering Chemistry, 18, 1582–1589.

Javadian H., Ghorbani F., Tayebi H., Asl S.M. H., 2013. Study of the adsorption of Cd (II) from aqueous solution using zeolite-based geopolymer, synthesized from coal fly ash; kinetic, isotherm and thermodynamic studies. Arabian Journal of Chemistry http://dx.doi.org/10.1016/j.arabjc.2013.02.018.

Kouamo Tchakoute H., Elimbi A., Diffo Kenne B.B., Mbey J.A., Njopwouo D., 2013. Synthesis of geopolymers from volcanic ash via the alkaline fusion method: Effect of Al_2O_3/Na_2O molar ratio of soda–volcanic ash. Ceramics International, 39, 269-276.

Sheng G.D., Shao D.D., Ren X.M., Wang X.Q., Li J.X., Chen Y.X., Wang X.K., 2010. Kinetics and thermodynamics of adsorption of ionizable aromatic compounds from aqueous solutions by as-prepared and oxidized multiwalled carbon nanotubes. Journal of Hazardous Materials, 178, 505–516.

Shoumkova A., Stoyanova V., 2013. Zeolites formation by hydrothermal alkali activation of coal fly ash from thermal power station ‘‘Maritsa 3’’, Bulgaria. Fuel, 103, 533–541.

Sommerville R., Blissett R., Rowson N., Blackburn S., 2013. Producing A Synthetic Zeolite From Improved Fly ash Residue. International Journal of Mineral Processing. http://dx.doi.org/10.1016/j.minpro.2013.07.005

Vereshchagina T.., Vereshchagin S., Shishkina N., Vasilieva N., Solovyov L., Anshits A., 2013. Microsphere zeolite materials derived from coal fly ash cenospheres as precursors to mineral-like aluminosilicate hosts for $^{135,137}Cs$ and ^{90}Sr. Journal of Nuclear Materials, 437, 11-18.

World Health Organization, 1993. Guidelines for drinking-water quality. 2^{nd} ed. Vol 1. Recommendations. Geneva: WHO.

Zhang X., Tang D., Jiang G., 2013. Synthesis of zeolite NaA at room temperature: The effect of synthesis parameters on crystal size and its size distribution. Advanced Powder Technology, 24, 689-696.