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KINETIC STUDY OF ADSORPTION OF HEAVY METALS ON BLAST FURNACE SLAG

ZORAN GLAVAŠ, ANITA ŠTRKALJ

University of Zagreb, Faculty of Metallurgy, Croatia
e-mail: glavaszo@simet.hr

In this paper, blast furnace slag was investigated as a potential adsorbent for the removal of zinc and copper ions from the aqueous solution. The adsorption was performed by a static, so-called "batch" process. Adsorption properties were studied by monitoring the influence of contact time adsorbent with adsorbate. Performed studies have shown that the equilibrium in the tested system is achieved in 30 minutes. Intraparticle diffusion model, heterogeneous diffusion model and film diffusion model were used to test the zinc and copper ion diffusion in a competitive adsorption. The obtained results showed that intraparticle diffusion controlled the adsorption process.
Key words: blast furnace slag, Cu(II) and Zn(II) ions, adsorption, kinetics.

Kinetička studija adsorpcije teških metala na visokopećnoj trosci. U ovom radu istraživana je visokopećna troska kao potencijalni adsorbens za uklanjanje iona cinka i bakra iz vodene otopine. Adsorpcija je provedena statičkim tzv. „batch“ postupkom. Adsorpcijska svojstva proučavana su praćenjem utjecaja vremena kontakta adsorbens/adsorbat. Istraživanja su pokazala da se ravnoteža u ispitivanom sustavu postiže za 30 minuta. Modeli međučestične difuzije, heterogene difuzije i difuzije kroz film upotrijebljeni su za ispitivanje difuzije iona cinka i bakra u kompeticijskoj adsorpciji. Dobiveni rezultati pokazuju da međučestična difuzija kontrolira proces adsorpcije.
Ključne riječi: visokopećna troska, Cu(II) i Zn(II) ioni, adsorpcija, kinetika.

INTRODUCTION

Heavy metals, such as arsenic, copper, zinc, lead, nickel, lead, cadmium, mercury, etc. in wastewaters represent a very serious environmental problem. Some of them are necessary for a large number of metabolic processes. However, in increased concentrations they can negatively affect the organism, cause serious disorders in the functioning of certain organs, and cause tumours and even death [1]. Therefore, it is extremely important to remove heavy metals from waste water before discharge into nature.

In practice, various methods, such as ion exchange, reverse osmosis, precipitation, membrane filtration, etc., are used to remove this problem. However, adsorption has been proved to be the best method. Adsorption is most often carried out using activated carbon as an adsorbent [2]. Although methods of removing heavy metals have been known for many years, they are still being investigated to improve as much as possible. This ultimately improves the process of removing heavy metals from waste water.

According to researches known in the literature [3], it is very often attempted to improve the adsorption method using various new adsorbents. Waste materials are often explored as potential adsorbens. Since wastes from some industries cannot be used further, their adsorption properties are being investigated. The use of waste materials as adsorbents has a beneficial effect on the environment because it reduces their amount at the landfill.

Metallurgical industry represents a great burden for the environment because it uses large amounts of energy and produces noise and large quantities of waste which sometimes depending on the type of waste cannot be recycled. Previous research has shown that wastes from metallurgical production, such as waste mould mixture, slag and carbon anode dust have good adsorption properties [4 – 6].

The kinetics of the adsorption process in which blast furnace slag was used as adsorbents and artificial waste water containing zinc and copper ions as adsorbate was studied in this article.

MATERIALS AND METHODS

Blast furnace slag generated in the production process of pig iron was used as adsorbent in this research. Characterization of the sample was performed by X-ray diffraction analysis and BET analysis. Adsorption was carried out by so-called "batch" method. To determine the kinetics of adsorption of Cu(II) and Zn(II) ion, 0.5 g of blast furnace slag (previously ground and dried to constant mass) and 50 ml of artificial waste water containing 25 ml of Cu(II) and 25 ml of Zn(II) ion solution was used. Initial solution concentrations of each ion were 100 mg/l. In order to determine the equilibrium time, the blast furnace slag and artificial waste water contact times were 5, 10, 15, 30, 60 and 90 minutes. Upon expiration of each contact time, the filtration was carried out using Whatman filter paper blue ribbon. In the obtained filtrates, Cu(II) and Zn(II) ion concentrations were determined by atomic absorption spectrometry. All experiments were performed as three parallel measurements at constant temperature and pH (22 °C and 5.63). Particle size of 0.125 to 0.2 mm was used for all experiments.

Adsorption capacity was calculated using equation (1) [7]:

$$q_e = \frac{c_0 - c_e}{m} \cdot V \qquad (1)$$

where is:

q_e – equilibrium capacity of adsorption of zinc and copper ions on blast furnace slag (mg/g),

q_t – adsorption capacity of zinc and copper ions on blast furnace slag after time t (mg/g),

c_0 –initial concentration of zinc and copper ions (mg/l),

c_e– equilibrium concentration of zinc and copper ions (mg/l),

m – weight of blast furnace slag (g),

V – volume of zinc and copper ions (l).

Film diffusion model, intraparticle diffusion model and heterogeneous diffusion model were used to describe the kinetic process (equations 2 – 5). The relative film diffusion rate is the slope of the linear part of curve presented by the equation (2) [7]:

$$\ln(1-F) = -\frac{3Dc}{r\delta c_a} t \qquad (2)$$

where is:

F- fraction of zinc and copper ions bonded in time t (dimensionless),

D- diffusion coefficient (mg/l),

c- concentration of zinc and copper ions in the solution(mg/l),

t – time (min),

r - particle radius (cm),

δ - film thickness (cm),

c_a- concentration of exchangeable zinc and copper ions on blast furnace slag (mg/l)

Value F was calculated from experimental results using the following equation [7]:

$$F = \frac{c_0 - c_t}{c_0 - c_e} \quad (3)$$

where is:
c_0 - initial concentration of zinc and copper ions in the solution (mg/l),
c_t - concentration of zinc and copper ions in the solution in time t (mg/l),
c_e- equilibrium concentration of zinc and copper ions in the solution (mg/l).

The heterogeneous diffusion model is represented by the equation (4) [7]:

$$F = \frac{1}{\delta} \ln t + C \quad (4)$$

where is:
δ- $\ln(\tau_m/\tau_i)$ (dimensionless),
τ_m- maximum value of τ (min),
τ_i- minimum value of τ (min),
τ - s^2/D (min),
s- maximum length of the diffusion path (m),
t – time (min),
C- integration constant.

The intraparticle diffusion model is represented by the equation (5) [7]:

$$F = a + \left(\frac{D}{r^2}\right)^{1/2} t^{1/2} \quad (5)$$

where is:
a - intraparticle diffusion constant (dimensionless),
D - diffusion coefficient (cm^2/s),

RESULTS AND DISCUSSION

The share of basic components in the blast furnace slag is shown in Table 1.

Table1. The share of basic components in the blast furnace slag
Tablica 1. Udio osnovnih komponenti u visokopećnoj trosci

Component	SiO_2	Al_2O_3	CaO	MgO
Share, %	33.19	11.59	42.76	4.75

According to the results of the BET analysis, the specific surface area of the blast furnace slag sample is 2.134 m^2/g, the volume of pores is 0.00166 cm^3/g and the mean pore diameter is 2.87. Figure 1 shows the influence of contact time on the competitive adsorption of Cu(II) and Zn(II) ions on the blast furnace slag.

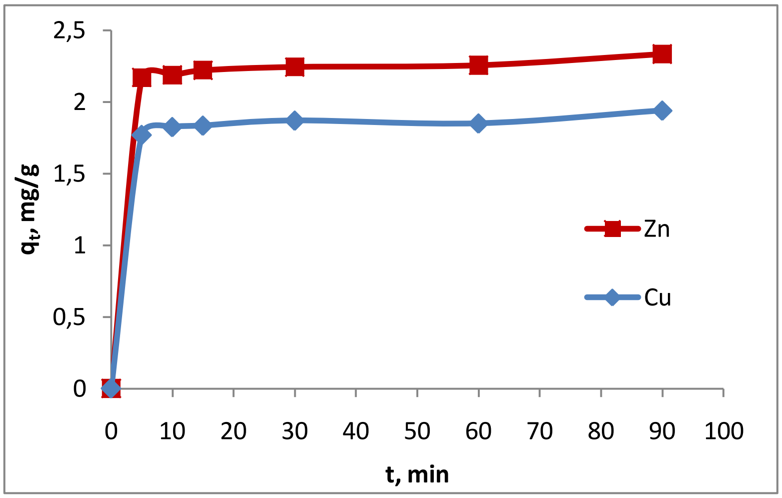

Figure 1. The influence of contact time on the competitive adsorption of Cu(II) and Zn(II) ions on the blast furnace slag

Slika 1. Utjecaj vremena kontakta na kompeticijsku adsorpciju Cu(II) i Zn(II) iona na visokopećnoj trosci

Figure 1 shows that adsorption kinetics for both ions in the mixture is very similar. The adsorption process takes place in three steps. The first step is relatively fast, the second is slightly slower and the third is almost stagnating. Adsorption equilibrium is achieved in 30 minutes for both ions in the mixture. The adsorption capacity of blast furnace slag at the equilibrium moment is slightly higher for zinc ions and is 2.24 mg/g. The equilibrium capacity of adsorption of copper ions on blast furnace slag is 1.87 mg/g. According to the studies available in literature [8, 9], such a way of adsorption is common because at the beginning of adsorption a large number of free places on adsorbent surface is available. With the progress of adsorption, free places are becoming more and more fulfilled. This means that the number of free places available for zinc and copper ions decreases. For this reason, the slowdown and the stagnation of the adsorption occur.

It is known that adsorption can take place in several different ways. The most common are film diffusion model, intraparticle diffusion model and hetero-geneous diffusion model. Identification of the steps in the adsorption process that determine the total removal rate is necessary for the interpretation of experimental data [7].

The results of measurement of adsorption of zinc and copper ions in the competitive adsorption on the blast furnace slag were processed by the above-mentioned models and they are shown in Figures 2 - 4.

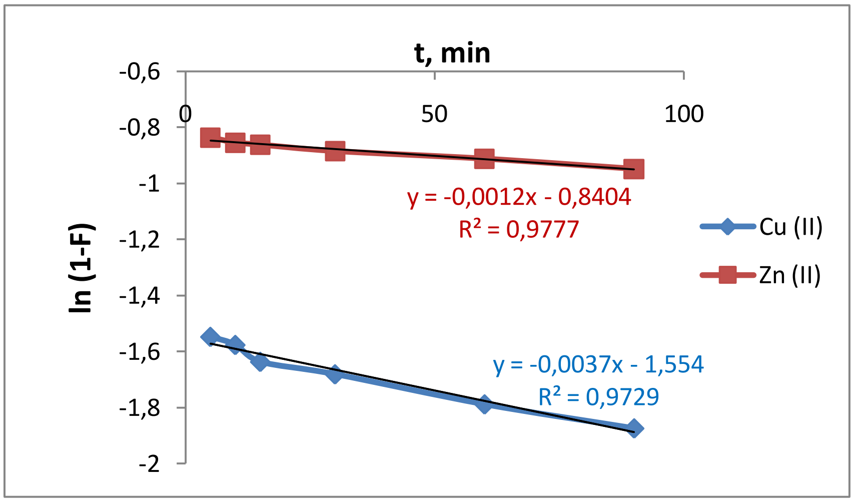

Figure 2. Film diffusion model for adsorption of zinc and copper ions on blast furnace slag
Slika 2. Model difuzije kroz film za adsorpciju iona cinka i bakra na visokopećnoj trosci

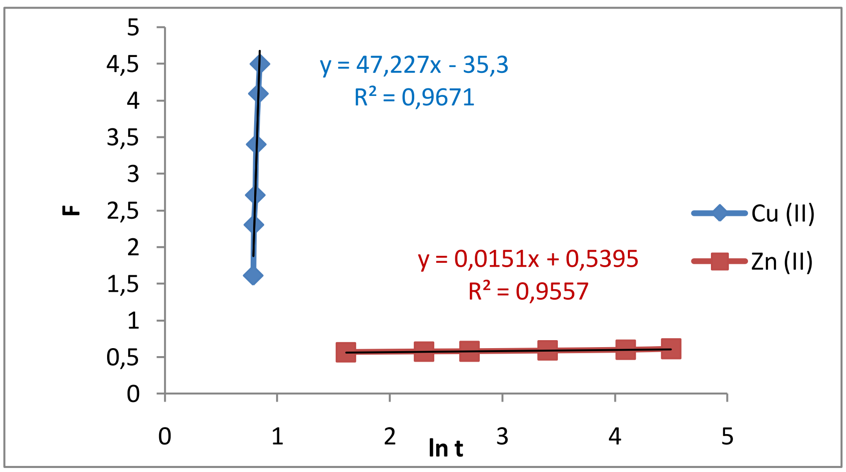

Figure 3. Heterogeneous diffusion model for adsorption of zinc and copper ions on blast furnace slag
Slika 3. Model heterogene difuzije za adsorpciju iona cinka i bakra na visokopećnoj trosci

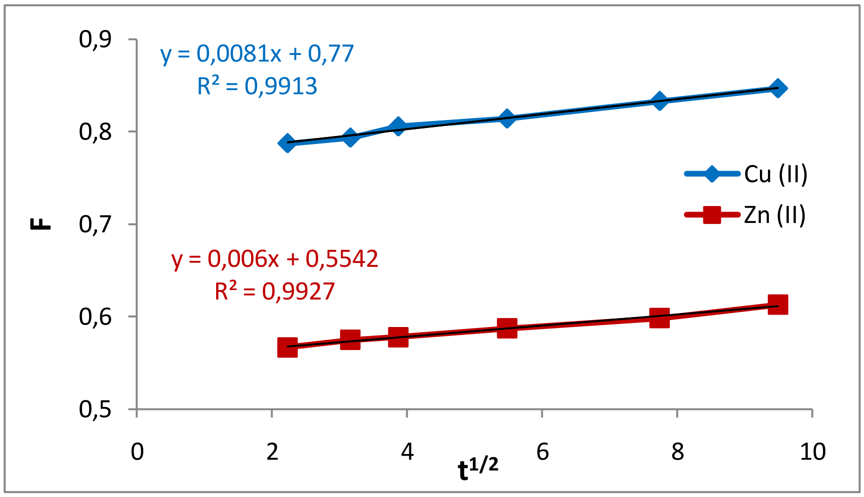

Figure 4. Intraparticle diffusion model for adsorption of zinc and copper ions on blast furnace slag
Slika 4. Model međučestične difuzije za adsorpciju iona cinka i bakra na visokopećnoj trosci

Generally it can be said that the transport of adsorbate from the solution onto the surface of the adsorbent particles takes place through a diffusion process in several steps -intraparticle, film and heterogonous diffusion. Transport is possible only by one step or a combination of several steps. In Figures 2 - 4 it can be seen that the coefficient of determination (R^2) ranges from 0.9557 to 0.9927 for zinc ion adsorption and from 0.9671 to 0.9913 for the copper ion adsorption. Since all values of R^2 are greater than 0.69, which indicates a strong correlation [10], it is likely that the adsorption takes place by a combination of three steps (intraparticle, diffusion film and heterogeneous). A somewhat higher coefficient of determination for adsorption of both ions on the blast furnace slag was obtained for the intraparticle diffusion model. This may indicate that this step can be accepted as a step that determines the rate of adsorption. However, to confirm this claim intraparticle diffusion rate constant should be in the range of 10^{-5} to 10^{-13} cm^2/s [11]. From the equation of the line in Figure 4, intraparticle diffusion rate constant for zinc ions is $9.3 \cdot 10^{-11}$ and intraparticle diffusion rate constant for copper ions is $1.6 \cdot 10^{-11}$. This confirms that the intraparticle diffusion is the step that determines the adsorption rate.

CONCLUSION

The obtained results show that waste from the production of pig iron, i.e. blast furnace slag, can be used as adsorbents for the adsorption of a mixture of zinc and copper ions from an aqueous solution. The value of the equilibrium capacity of adsorption is 2.24 mg/g for the zinc ions and 1.87 mg/g for copper ions. This confirms that blast furnace slag can be used as a potential adsorbent. The kinetics of adsorption of the investigated system takes place in three steps. The first is relatively fast, the second is slower and the third is stagnant. Equilibrium adsorption of mixture of zinc and copper ions on the blast furnace slag is achieved very quickly, during 30 minutes for both tested ions. It is also likely that the adsorption takes place by a combination of all three forms of diffusion, intraparticle, film and heterogonous diffusion. However, according to the obtained results it can be concluded that the intraparticle diffusion is the step that determines the adsorption rate.

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