WASTE MOLDING SAND AS AN AGENT FOR THE REMOVAL OF Cu(II) AND Zn(II) IONS FROM AQUEOUS SOLUTION

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Abstract

This article presents the application of non-hazardous waste molding sand from gray cast iron foundry as an inexpensive adsorbent for removal of Zn(II) and Cu(II) ions from aqueous solutions. The experiments were performed at room temperature using a multi solution (Zn + Cu) with concentration was 100 mg/l. The process of removal of Zn(II) and Cu(II) ions was monitored at different contact times of waste molding sand and metal ions. The experimental data were processed by two different kinetic theories. The pseudo-first-order and pseudo-second-order models were used for modeling the kinetic rates.

Obtained results show that the waste molding sand has significant potential for the removal of Zn(II) and Cu(II) ions from aqueous solutions. Research shows that the removal of Cu(II) ions was better than removal of Zn (II) ions. It is possible to conclude that the mutual competition of Cu(II) and Zn(II) ions for adsorption sites affect the intensity of their removal.

KEYWORDS: WASTE MOLDING SAND, Zn(II) IONS, Cu(II) IONS, ADSORPTION

1. Introduction

There are many factors that influenced the development of new ways for sustainable development, such as: a large amount of various industrial wastes, environmental pollution and high consumption of natural resources. Achieving sustainable development is possible only with an increase in resource efficiency. This is possible if we reduce the consumption of materials and energy. Therefore, it is beneficial to use a variety of by-products or solid wastes from industries. For example, in the production of concrete it is possible to use slag from metallurgical aggregates and waste mold sand from foundries. Production costs and environmental problems were reduced by this approach. Resulting concrete has adequate quality and environmental acceptability [1].

By-products from the production process create significant difficulties for foundries. If we take into account all the by-products from the foundry, more than 70% relates to the foundry sand which is used for mold making [2].

Different binders are used for binding of grains of foundry sand. Expendable molds are widely used in production of metal castings. They are usually produced from clay-bonded (green) sand or chemically bounded sand. Clay-bonded (green) sand for molds consists of silica sand (80 – 95%), bentonite clay (4 – 10%), water (2 – 5%) and carbonaceous additives (2 – 10%). Chemically bonded sand consists of silica sand and chemical binder (1 – 3%). It is used for making molds and cores. Chemical binder is mixed with silica sand. The chemical reaction which occurs under the effect of the catalyst results in curing of the mixture. For making mold and cores in foundries, different chemical binders are used, such as: sodium silicate, furfuryl alcohol, phenolic resins, alkyd oil type resin etc. [2].

When the properties of sand become unsuitable for further use, such sand is called waste foundry sand and removed from the foundry [1].

2. Prerequisites and means for solving the problem

In the production process of one ton of cast metal, approximately one ton of waste is produced. [3]. Safe disposal of waste materials is a demanding task, which is important as maintaining the quality and profit. Therefore, efforts should be made to reduce the amount of waste materials through reuse or use for other purposes. In this context, the use of foundry waste molding sand as the adsorbent for heavy metals from wastewater is very interesting. In addition, this approach reduces the cost of disposal of waste materials.

In the process of adsorption, adsorbate molecules are concentrated on the surface of the adsorbent.

The molecules of adsorbate come from the bulk phase and being adsorbed in the pores in the partially liquid state. The ratio of the concentration to the solubility of the compound is the driving force for adsorption. Detailed research of adsorption, adsorption kinetics and equilibrium, as well as influential parameters, such as temperature, pH, surface area, etc. was performed by Dound [4]. Adsorption is a useful and economical method at low concentrations of pollution. In comparison to membrane filtration or ion exchange and other conventional methods, the adsorption has advantages, such as low cost, easy to perform, efficiency, availability, low cost and environment friendly [5-8]. Recently, a lot of research has been done on the use of inexpensive and easily available materials in wastewater treatment. Currently, the adsorbent which is most often used in wastewater treatment is the activated carbon. However, the activated carbon is expensive. Therefore, intensive research performs on the use of inexpensive and available materials (particularly waste materials), as a substitute for the activated carbon [9].

This paper presents the possibility of using sodium-silicate-bonded sand (chemically bound mixture) for the adsorption of Cu (II) and Zn (II) ions from aqueous solutions. The adsorption process is presented by kinetic models.

3. Solutions of the examined problem

Waste sodium-silicate-bonded sand used in the present study was obtained from foundry and had the following chemical composition: 91 % SiO_2, 2.1 % Al_2O_3, 9.6 % Fe, 0.4 % Mg, 0.05 % Ni, 0.03 % Cr, 0.76 % C and 0.02 % Mn.

A stock solutions of Cu(II) and Zn(II) for batch adsorption experiment were obtained by dissolving the exact quantity of $CuSO_4{\cdot}5H_2O$ and $ZnCl_2$ in ultra pure water. The test solutions containing single ions were prepared by diluting 1000 mg/L of stock solutions of metal ions to the desired concentrations. For the investigation with binary solutions, the desired combinations of 100 mg/L Cu(II) and 100 mg/L Zn(II) ions were used.

Waste foundry sand (sodium-silicate-bonded sand) in an amount of 1 g, 25 ml of the Cu (II) ions and 25 mL of the Zn (II) ions were mixed for study of the adsorption process. The kinetics of the process is monitored in a time of 10, 20, 30, 40, 50 and 60 minutes.

The concentrations of Cu(II) and Zn(II) ions in solution after adsorption were determined by spectrometric method (Atomic Adsorption Spectrometry with graphite furnace). Before that, the samples were filtered (Whatman- blue ribbon filter).

The kinetics of Cu(II) and Zn(II) ions adsorption was modeled applying the first- and second-order kinetics models [10].

The pseudo-first-order (Lagergen`s model) equation is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g), k_1 is the rate constant of pseudo first-order adsorption (1/min).

The pseudo-second-order (Ho`s model) equation is expressed by the following formula:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2}$$

where k_2 is the rate constant of pseudo-second-order adsorption (g/(mg·min)).

The fitting of the all models (isotherms and kinetics) was performed using regression analysis. Performance of the models to the experimental data was checked by comparison of the correlation coefficient r^2.

4. Results and discussion

Kinetic analysis of adsorption represents the determination of the amount of adsorbed substance depending on time [11].

The obtained results for the adsorption of Cu(II) and Zn(II) ions per unit mass of waste foundry sand as a function of time are shown in Figure 1. It shows that the adsorption capacity q_t increases very rapidly in the beginning of process. Maximum capacity is achieved in 30 minutes for both investigated ions. These results indicate that the kinetics of fixing Cu(II) and Zn(II) ions on waste foundry sand surface was fast. It is assumed that the cause of this rapid adsorption was a sufficient number of places on the surface of the adsorbent. When the system reaches equilibrium state, free places on waste foundry sands are probably filled in. Adsorption capacity of Cu (II) ions at the time of achieving equilibrium was 2.465 mg/g, while the adsorption capacity of Zn (II) ions was smaller (2.335 mg/g). Different adsorption capacities may be associated with various radius of ions. The ionic radius of Cu is smaller, which allows faster and more easily positioning of this ion to the free places on the investigated adsorbent. Similar observations were presented by the other authors who have studied different adsorption systems [12-14].

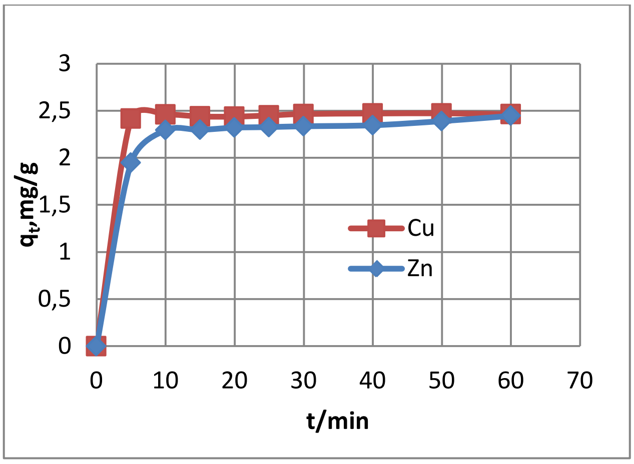

Fig. 1 *Dependence of adsorption capacity on the time of contact of the investigated system of waste foundry sands/binary solution Cu (II)-Zn (II) ions*

The obtained kinetic results were modeled using pseudo first model and pseudo-second order kinetics models (Figures 2 and 3).

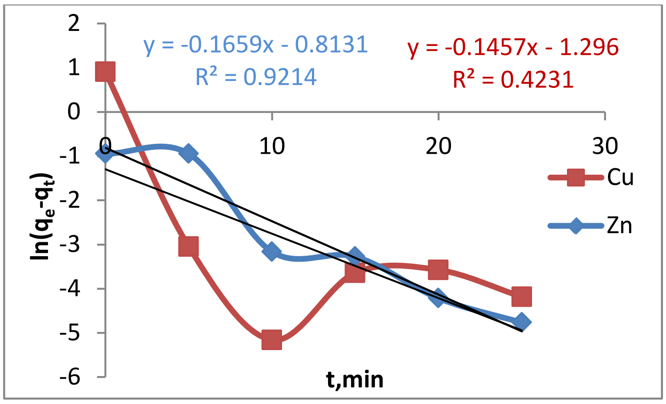

Figure 2. Pseudo-first order kinetics plots for the adsorption of Cu(II) and Zn(II) ions on waste foundry sand

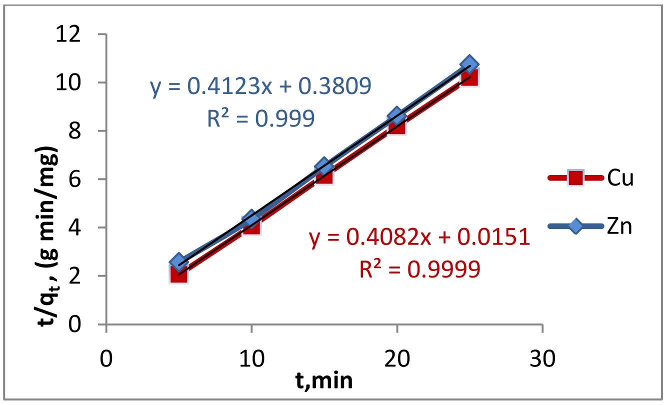

Fig. 2 *Pseudo-second order kinetics plots for the adsorption Cu(II) and Zn(II) ions on waste foundry sand*

Table 1 contains the constants and correlation coefficients for the kinetic models of adsorption of Cu(II) and Zn(II) ions on waste foundry sand.

Table 1: *Constants and correlation coefficients of kinetic models for the adsorption of Cu(II) and Zn(II) ions on waste foundry sand*

Pseudo-first order		
	Cu(II)	Zn(II)
$q_{e,\ exp}$ [mg/g]	2.466	2.335
$q_{e,theor.}$ [mg/g]	-	-
k_1 [1/min]	0.1451	0.1659
R^2	0.4231	0.9214
Pseudo-second order		
	Cu(II)	Zn(II)
$q_{e,\ exp}$ [mg/g]	2.466	2.335
$q_{e\ theor}$ [mg/g]	2.450	2.425
k_2 [g/(mg·min)]	11.033	0.446
R^2	0.9999	0.999

Comparison of the correlation coefficients in Table 1 shows that the correlation coefficients for the pseudo-second order kinetics (R^2=0.9999 for Cu(II) and R^2=0.999 for Zn(II)) are higher than for the pseudo-first order kinetics (R^2=0.4231 for Cu(II) and R^2=0.9214 for Zn(II)). This fact indicates that the adsorption of the Cu(II) and Zn(II) ions was performed according to the reaction kinetics of the second order. Furthermore, a comparison between the experimental adsorption capacities ($q_{e,exp}$) and modeled adsorption capacities ($q_{e,theor.}$) shows that the modeled adsorption capacities from pseudo second order model very well correspond to the experimental with a small**.** The modeled adsorption capacity for the pseudo-first order kinetics could not be calculated. This also contributes to the previously mentioned fact.

The constant for the pseudo-second order kinetics of the adsorption Cu(II) ions on waste mould sand has a higher value in relation to the constant for the pseudo-second order kinetics of the adsorption Zn(II) on waste foundry sand. This is also further proof that the adsorption of Cu(II) on waste foundry sand is better than adsorption of Zn(II).

5. Conclusion

- The obtained adsorption capacities for systems waste foundry (mould) sand/binary system Cu(II)-Zn(II) ions are a good indicator of waste foundry sand potential for use in aqueous adsorption system.
- Adsorption equilibrium was achieved very quickly, for 30 minutes.
- The results indicate that the kinetics of Cu (II) and Zn (II) ions on waste foundry sand can be described by the pseudo-second order kinetics model.
- Comparing the kinetic constants (k_2Cu(II)= 11.033 g/(mg·min) , k_2Zn(II)= 0.446 g/(mg·min)) it is possible to conclude that the adsorption of Cu (II) ions o waste foundry sand is better than the adsorption of Zn (II) ions.

6. References

[1] Aggarwal Y., Siddique R. Microstructure and properties of concrete using bottom ash and waste foundry sand as partial replacement of fine aggregates, Construction and Building Materials, 54(2014), 210-223.

[2] Singh, G., Siddique R. Effect of waste foundry sand (WFS) as partial replacement of sand on the strength, ultrasonic pulse velocity and permeability of concrete, Construction and Building Materials, 26(2012), 416-422.

[3] …, ASM Handbook, Volume 15, Casting, ASM International, Materials Park, Ohio, 2008.

[4] Duond D. D., Adsorption Analysis: Equilibria and Kinetics, London, Imperial College Press, 1998.

[5] Cheremisinoff N. P., Handbook of Water and Wastewater Treatment Technologies, Boston, Butterworth-Heinemann, 2002.

[6] Aeisyah S. N., Halim A. M.., Ismail S., Kamal and L., Izhar S., Adsorption Process of Heavy Metals by Low-Cost Adsorbent: A Review, World Applied Sciences Journal 28(2013)11, 1518-1530.

[7] Okoli J., Ezuma I., Adsorption Studies of Heavy Metals by Low-Cost Adsorbents, Journal of Applied Sciences and Environmental Management, 18(2014)3, 443-448.

[8] Kothiyal N. C., Sharma S., Removal of Cr (VI) from Aqueous Solution by Polymer Based Guar Gum G-poly (AAm) and activated charcoal adsorbents, The Holistic Approach to Environment 2(2012)1, 3-22

[9] Owlad M., Aroua M. K., Dau W., Baroutian S., Removal of Hexavalent Chromium-Contaminated Water and Wastewater: A Review, Water Air Soil Pollution, 200(2009)1-4, 59-77.

[10] Šipuš I., Štrkalj A., Glavaš Z., Removal of Cr (VI) ions from aqueous solution using foundry waste material: Kinetic and equilibrium studies, Canadian Metallurgical Quarterly, 51(2012)4, 413-418.

[11] Aarden F. B., Adsorption on Heterogeneous Porous Materials, Equilibrium and Kinetics, Eindhoven, Technische Universiteit, 2001.

[12] Ho Y., Pseudo-Isotherms Using a Second Order Kinetic Expression Constant, Adsorption, 10(2004), 151–158.

[13] Hossain M.A , Ngo H. H., Guo W. S., Nghiem L. D., Hai F. I., Vigneswaran S., Nguyen T. V., Competitive adsorption of metals on cabbage waste from multi-metal solutions, Bioresource Technology, 160(2014), 79–88

[14] Cabrera-Lafaurie W. A., RománF. L., Hernández-Maldonado A. J., Single and multi-component adsorption of salicylic acid, clofibric acid, carbamazepine and caffeine from water onto transition metal modified and partially calcined inorganic–organic pillared clay fixed beds, Journal of Hazardous Materials, 282(2015), 174–182.