www.czasopisma.pan.pl PAN POLSKA AKADEMIA NAUK www.journals.pan.pl

Arch. Metall. Mater., Vol. 61 (2016), No 4, p. 1805–1812

DOI: 10.1515/amm-2016-0292

A. STRKALJ*,#, Z. GLAVAS*, L. SLOKAR*

MICROSTRUCTURAL AND EQUILIBRIUM ADSORPTION STUDY OF THE SYSTEM OF WASTE FOUNDRY MOLDING SAND/Cu (II) IONS

This paper deals with the waste foundry molding sand which originally comes from the casting production. Adsorption of Cu (II) ions on the waste foundry molding sand was studied. Experimental data were processed using adsorption isotherms. Obtained results show that the experimental data are best described by the Langmuir isotherm. The following adsorption capacities are obtained: 7.153 mg/g to 293 K, 8.403 mg/g at 333 K and 9.208 mg/g at 343 K. The kinetics and thermodynamics of the process were analysed. The obtained results indicate that the adsorption process takes place according to the pseudo second order kinetic model with the following constants: 0.438 g/mg min at 293 K, 0.550 g/mg min at 333 K and 1.872 g/mg min at 343 K. The following values of Δ*G*° were obtained: - 95.49 J/mol at 293 K, - 736.99 J/mol at 333 K and - 1183.46 J/mol at 343 K. The value of Δ*H*° is - 4.16 kJ/mol and the value of Δ*S*° is 15.17 J/molK. These results were confirmed by microscopic examinations. The results indicate that the adsorption process of Cu (II) ions on waste foundry molding sand is possible. Results of microscopic examinations show the homogeneity of the surface, which is proof of the chemisorption. Cu (II) ions on the surface of the waste foundry molding sand were detected after adsorption by EDS analysis, which proves the existence of the adsorption process.

Keywords: waste foundry molding sand, Cu (II) ions, adsorption, SEM/EDS analysis

1. Introduction

Environmental pollution, a large amount of various wastes from industries and high consumption of natural resources are just some of the factors which require finding new paths for sustainable development. Increasing resource efficiency is crucial for achieving sustainable development. Therefore, it is necessary to reduce the consumption of energy and materials. In this context, it is useful to use various by-products and waste materials from industries.

The molds for the production of iron castings are usually made from foundry molding sands. In essence it is a mixture consisting of silica sand (> 90 %), a binder and various additives (for example coal dust, rice hulls, wood flour etc.) to enhance the properties of a mixture [1-3]. Bentonite clays are most commonly used binder. Foundry molding sand containing such binder is known as green sand. This sand is used several times for mold making. After a few cycles of use, it becomes waste. Many waste foundry molding sands, especially those from the foundries of iron and aluminium castings, are used again for a different purposes, e.g. in the production of cement/concrete and asphalt, then in the construction of roads, embankments, etc. [4]. Recently it is used in removal process of heavy metals from the waste water, since it is not a hazardous waste [5 - 7]. This approach reduces the environmental problem pollution and production costs. Researchers have used the waste foundry molding sand to remove paints, Zn (II), Cr (VI) and Cu (II) ions [8 - 14]. The obtained results were described by adsorption isotherms, kinetics and thermodynamics of adsorption. Comparing the results it is evident that until now researched adsorption processes on waste foundry molding sand are taking place according to Langmuir isotherm with adsorption capacities ranging from 3.31 to 23.29 mg/g and according to pseudo second order kinetic model.

Copper in low concentrations is beneficial to the human body. However, in higher concentrations can cause many health problems. Accidental ingestion can result in acute toxicity with copper. Because of the disease or genetic predisposition certain people may be more susceptible on harmful effects of high intakes of copper. Copper can be indirectly linked to various neurological disorders, such as Alzheimer's disease and prion diseases, including bovine spongiform encephalopathy [15]. Therefore, it should be removed from waste water before discharge into the environment. According to Croatian regulation, allowed copper concentration in waste water is 0.5 mg/L [16].

In this paper, the adsorption of Cu (II) ions on the waste foundry molding sand was studied. Adsorption process is described by using two isotherm equilibrium models (Freundlich and Langmuir) and by two kinetic models (pseudo first and pseudo second order). Thermodynamics of adsorption of the analysed system is also determined. Microstructure of samples before and after adsorption process was investigated by light and scanning electron microscope coupled with energy-dispersive spectrometer.

---

* UNIVERSITY OF ZAGREB, FACULTY OF METALLURGY, ALEJA NARODNIH HEROJA 3, 44103 SISAK, CROATIA

Corresponding author: strkalj@simet.hr

Unlike until now performed researches, different parameters of the adsorption process (ratio of adsorbent/adsorbate, contact time, temperature, pH) were selected in this paper. In addition, the microstructure of waste foundry molding sand and morphologies of the surface were analysed and present elements were detected by using light and scanning electron microscope coupled with energy-dispersive spectrometer.

2. Materials and methods

Waste bentonite clay bonded foundry molding sand from the gray and ductile iron foundry was used in this study. Its chemical composition is presented in Table 1.

TABLE 1

Chemical composition of the used waste foundry molding sand

Compound	SiO_2	Al_2O_3	Fe	Mg	Ni	C	Mn
Content, wt. %	91	2.1	6.3	0.04	0.04	0.5	0.02

Using the nitrogen adsorption method, the BET surface area of the waste bentonite clay bonded foundry molding sand was determined (4.33 m^2/g). The pore volume (0.0134 cm^3/g) and pore diameter (11.28 nm) were also determined.

2.1. Batch experiments

A representative sample of waste foundry molding sand for the analysis was obtained by a quartering technique. It was dried at 105 °C for 4 hours. Adsorption studies were carried out by batch technique. Waste foundry molding sand in an amount of 1 g was put in a plastic cups and is used as the adsorbent. Adsorbate was prepared by diluting a stock solution of Cu (II) ions (1000 mg/L) in order to obtain concentrations of 2, 6, 10, 20, 60 and 100 mg/L. Adsorption system of waste foundry molding sand/Cu (II) ions (1 g/50 mL) was studied for 5, 10, 20 and 30 minutes at 297, 333 and 343 K without corrections of pH (initial pH value was 6.15).

Filtration was carried out after 30 minutes. The amount of Cu (II) ions removed by waste foundry molding sand was determined as the difference between the initial concentration of Cu (II) ions and concentrations of Cu (II) ions in the filtrate. Concentrations of Cu (II) ions in filtrates were determined by atomic adsorption spectrometer with graphite furnace (Analytic Jena, ZEEnit 650). All experiments were carried out twice. Mean values were calculated and used for further calculations.

Adsorption data were described by two adsorption isotherms – Langmuir and Freundlich. The linear form of the Langmuir equation can be shown as follows:

$$\frac{1}{q_e} = \frac{1}{K_L \cdot q_m \cdot c_e} + \frac{1}{q_m} \qquad (1)$$

where q_e is the amount of adsorbed Cu (II) ions (mg/g), c_e is the equilibrium concentration of Cu (II) ions (mg/L) and q_m and K_L are Langmuir constants associated with the maximum capacity of adsorption (mg/g) and energy of adsorption (L/mg).

The linear form of the Freundlich equation can be shown by the following equation:

$$lnq_e = lnK_F + \frac{1}{n} \cdot lnc_e \qquad (2)$$

where q_e is the amount of adsorbed Cu (II) ions at equilibrium (mg/g), K_F is the Freundlich constant, 1/n is the heterogeneity factor which is associated with the capacity and intensity of the adsorption and c_e is the equilibrium concentration of Cu (II) ions (mg/L).

The two kinetic models were used to describe the kinetics of the adsorption process. Pseudo first model equation can be shown by the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \qquad (3)$$

Pseudo second model equation can be shown by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \qquad (4)$$

where q_e is the amount of adsorbed Cu (II) ions at equilibrium (mg/g), q_t is the amount of adsorbed Cu (II) ions at time t (mg/g), k_1 and k_2 are kinetic constants (min^{-1} and g/mg·min) and t is time, min.

Thermodynamics of the process can be shown by the following equation:

$$lnK_L = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (5)$$

where $\Delta G°$ is change of standard free energy (J/mol), $\Delta H°$ is change of enthalpy (kJ/mol), $\Delta S°$ is change of entropy (J/molK), K_L is Langmuir constant (L/mg) and T is temperature (K).

2.2. Microscopic examinations

Samples for microscopic examinations were prepared by mixing waste foundry molding sand (before and after adsorption process) with KBr, followed by pressing to obtain a disk shape (diameter: 3 mm, height: 2 mm) using the Shimadzu hand press. Thereafter, the samples in the form of a disk were mounted in a conductive mass. Stereo microscope Olympus SZ11 with digital camera was used to observe the microstructure of waste foundry molding sand. Grain size number G was determined according to standard ASTM E112-96 using a microscope Olympus GX51 with image analysis software. Scanning electron microscope Tescan SEM Vega LSH (TS 5130 LS) equipped with Bruker energy-dispersive spectrometer (EDS) was used to analyse the surfaces morphologies and detection of present elements.

3. Results and discussion

data on the adsorption equilibrium is the most important information for the understanding of the adsorption process. Adsorption equilibrium of the system of waste foundry molding sand/Cu (II) ions is shown in Figure 1.

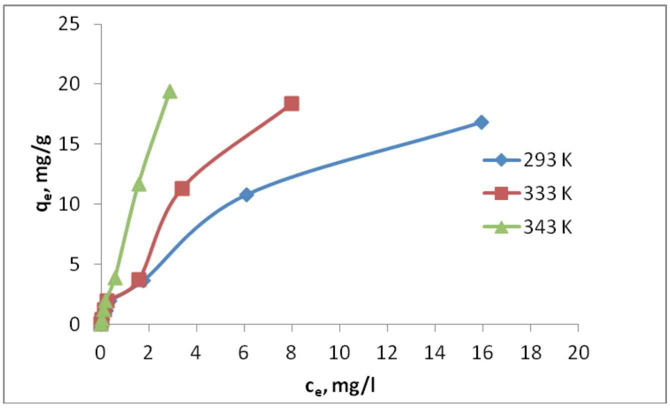

Fig. 1. Adsorption equilibrium of the system of waste foundry molding sand/Cu (II) ions

Freundlich and Langmuir adsorption isotherms for the system of waste foundry molding sand/Cu (II) ions are shown in Figures 2 and 3.

Typical adsorption parameters determined from the isotherms equations are given in Table 2.

The coefficient of determination (r^2) was used to select the isotherm that best describes the experimental data. All coefficients of determination are very high (0.9723 - 0.9956). This indicates the possibility of describing the experimental data using both isotherms (Freundlich and Langmuir). However, the r^2 values of Langmuir isotherm are a little higher.

For a description of adsorption characteristics of the heterogeneous surface, Freundlich isotherm is usually used. This isotherm quantitatively describes formation of adsorbate monolayer on the external surface of the adsorbent. Further adsorption does not occur thereafter. Adsorption capacity can be estimated based on the constant KF. Factor *1/n* provides information on the strength of adsorption in the adsorption process [17]. The distribution between the two phases is not dependent on the concentration if $n = 1$. Normal adsorption occurs if $n < 1$. In the case of $n > 1$, cooperative adsorption is taking place [18]. Function reaches an asymptotic maximum along with increasing pressure without bound. The constants (K_F and n) are changing along with temperature increase. The adsorbed quantity increases slowly. In order to saturate the surface, higher pressures are necessary. The parameters KF and n are parameters specific to the adsorbent-adsorbate system. They must be determined when the linear regression is used to determine the parameters of the kinetics and isotherm models. For correlation of adsorption data, linear least-square method and linearly transformed equations are commonly used. $1/n$ represents the heterogeneity parameter. The heterogeneity increases with decreasing of parameter $1/n$. When $n = 1$, it is a linear adsorption isotherm. If $1 < n < 10$, we can expect a favourable adsorption process [19].

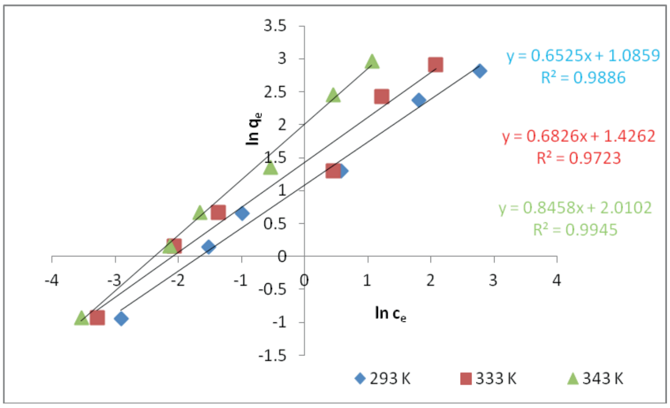

Fig. 2. Freundlich adsorption isotherm for the system of waste foundry molding sand/Cu (II) ions

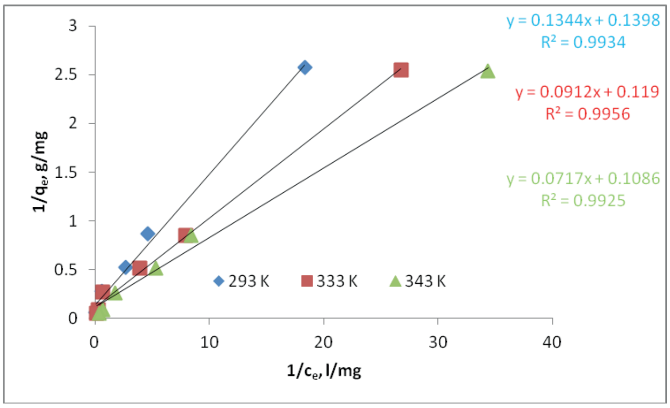

Fig. 3. Langmuir adsorption isotherm for the system of waste foundry molding sand/Cu (II) ions

The equilibrium distribution of metal ions between liquid and solid phase is shown by the Langmuir isotherm [20]. This type of isotherm is suitable for adsorption in a single layer on the surface that has a fixed number of the same places. Energies of adsorption on the surface are uniform according to this model. There is no transmigration of adsorbate in the surface plane. Separation factor or equilibrium parameter R_L is used to represent important features of the Langmuir isotherm [21]. This dimensionless constant can be shown by the following equation:

TABLE 2

Freundlich and Langmuir adsorption constants for the system of waste foundry molding sand/Cu (II) ions

	Freundlich isotherms			Langmuir isotherms		
T/K	*1/n*	K_F	r^2	q_m(mg/g)	K_F(L/mg)	r^2
293	0.6525	2.962	0.9886	7.153	1.040	0.9934
333	0.6826	4.163	0.9723	8.403	1.305	0.9956
343	0.8458	7.465	0.9945	9.208	1.515	0.9925

$$R_L = \frac{1}{1+(1+K_L c_0)} \qquad (6)$$

where c_0 is initial concentration (mg/L), K_L is Langmuir constant (associated with the energy of adsorption) (L/mg). In the case of $0 < R_L < 1$, adsorption is favourable. If $R_L > 1$, adsorption is not favourable. Adsorption is linear if $R_L = 1$, or irreversible if $R_L = 0$. Langmuir isotherm is favourable in this research, because the value of the parameter R_L is in the range between 0 and 1 ($R_L = 0.009$). This indicates that the equilibrium adsorption was favourable.

Figure 4 shows the experimental kinetic data for adsorption.

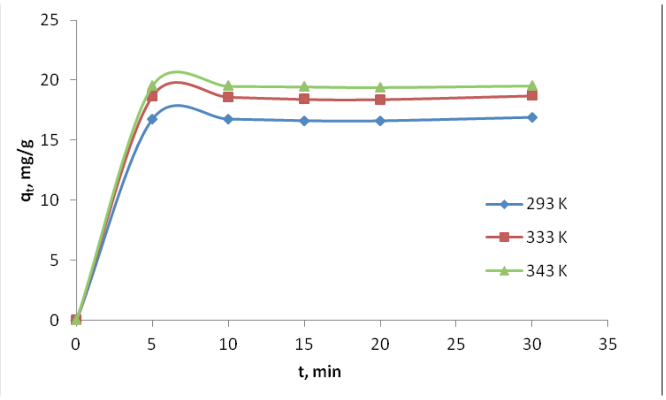

Fig. 4. Effect of time and temperature on the adsorption capacity of the waste foundry molding sand

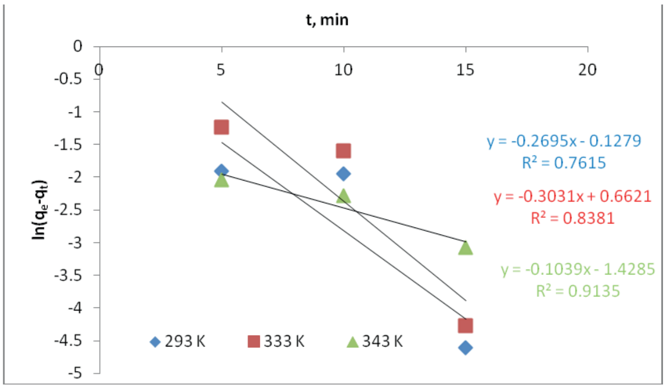

Fig. 5. Linearized shape of pseudo first order kinetic model for system of waste foundry molding sand /Cu (II) ions

Figure 4 shows that an increase in adsorption time was resulted in increase of the adsorption of Cu (II) ions, regardless of the applied temperature. After 20 min. adsorption equilibrium was obtained. The curves show a high rate of adsorption in the first several minutes of the process.

Figures 5 and 6 show the linearized shape of pseudo first and pseudo second order models for the initial concentration of Cu (II) ions of 100 mg/L at three applied temperatures.

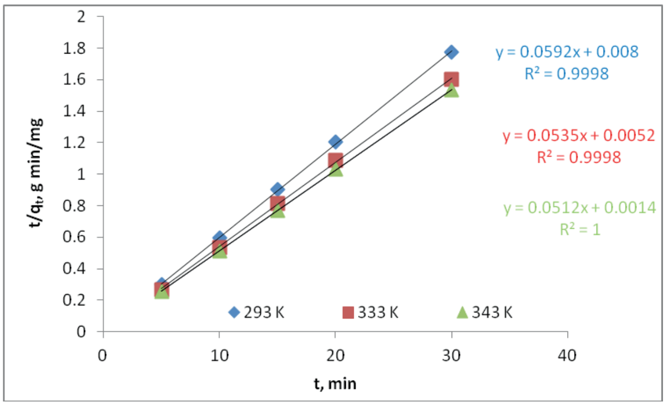

Fig. 6. Linearized shape of pseudo second order kinetic model for system of waste foundry molding sand /Cu (II) ions

The kinetic constants of the adsorption system of waste foundry molding sand/Cu (II) ions are shown in Table 3.

The data in Table 3 show that the values of q_e obtained by using the pseudo first order model are significantly different from the values of q_e measured experimentally. This indicates that the adsorption is not a pseudo first order reaction. In addition, the coefficients of determination (r^2) for the pseudo first order model are lower than the coefficients of determination (r^2) for the pseudo second order model.

Furthermore, in Table 3 it can be seen that the second order rate constant increases with increase in temperature. This suggests that the adsorption of Cu (II) ions on the waste foundry molding sand is activated process. The second order kinetic model has a very high coefficient of determination (r^2) for all applied temperature. In addition, there is a very good agreement between the theoretical values of q_e and experimentally measured. Based on these facts, it can be concluded that the adsorption of Cu (II) ions takes place according to the second order kinetic model.

The temperature dependence of second order rate constant can be shown by the following equation:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \qquad (7)$$

where k_2 is the adsorption rate constant, A is a constant called the frequency factor, E_a is the activation energy (kJ/mol), R is the gas constant (8.314 J/molK) and T is the temperature (K).

The adsorption activation energy is 12.7 kcal/mol, and it is determined from the slope of the plot (equation (7)). It follows

TABLE 3

Kinetic constant of adsorption system of waste foundry molding sand/Cu (II) ions

T/K	Pseudo first order			Pseudo second order		
	q_e (mg/g)	k_1 (min^{-1})	r^2	q_e (mg/g)	k_2(g/mg min)	r^2
293	0.880	0.2695	0.7615	16.892	0.438	0.9998
333	1.939	0.3031	0.8381	18.691	0.550	0.9998
343	0.240	0.1039	0.9135	19.531	1.872	1

that the adsorption of ions on the waste foundry molding sand is activated process. This confirms the chemical nature of the process (i.e. chemisorption) [22].

Thermodynamic parameters of an adsorption process (ΔG°, ΔH° and ΔS°) also indicate nature of the process (Table 4). Generally, if the value of the parameter ΔG° is around 20 J/mol, adsorption is physical nature. If the value of $\Delta G^\circ < -40$ J/mol, it is a chemisorption. In addition, the negative value of ΔG° indicates a spontaneous adsorption process. If parameter ΔH° has a negative value, it is the exothermic adsorption process. Increased randomness during adsorption is present if the value of the parameter ΔS° is positive [23, 24].

Table 4 shows that the adsorption of Cu (II) ions on the waste foundry molding sand takes place spontaneously and has a chemical nature. The value of ΔH° is negative, which means that the adsorption is exothermic. The value of ΔS° is 15.17 J/molK, indicating an increased randomness during adsorption of Cu (II) ions on waste foundry molding sand.

TABLE 4

Thermodynamic parameters for system of waste foundry molding sand sand/Cu (II) ions

T/K	$-\Delta G^\circ$ (J/mol)	$-\Delta H^\circ$ (kJ/mol)	ΔS° (J/molK)
293	95.49	4.16	15.17
333	736.99		
343	1183.46		

The results obtained in this research are comparable to the results in the literature [11, 25].

The adsorbed Cu (II) ions were also visible in a microstructure of the waste foundry molding sand. Namely, observation of microstructure by light microscope was performed before and after adsorption process and obtained micrographs are shown on Figure 7.

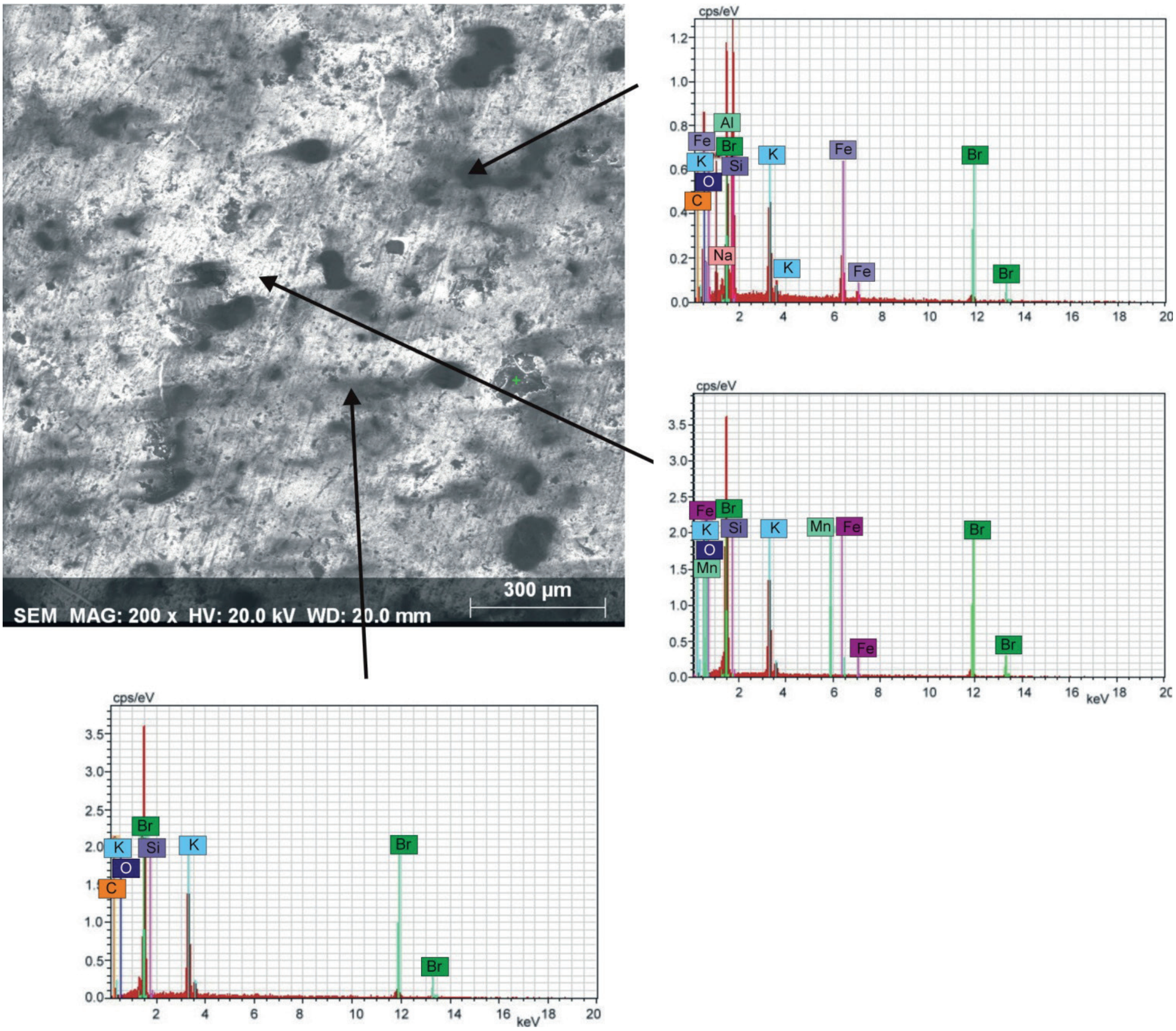

Fig. 8. SEM micrograph and EDS spectrum of elements in waste foundry molding sand before the adsorption process

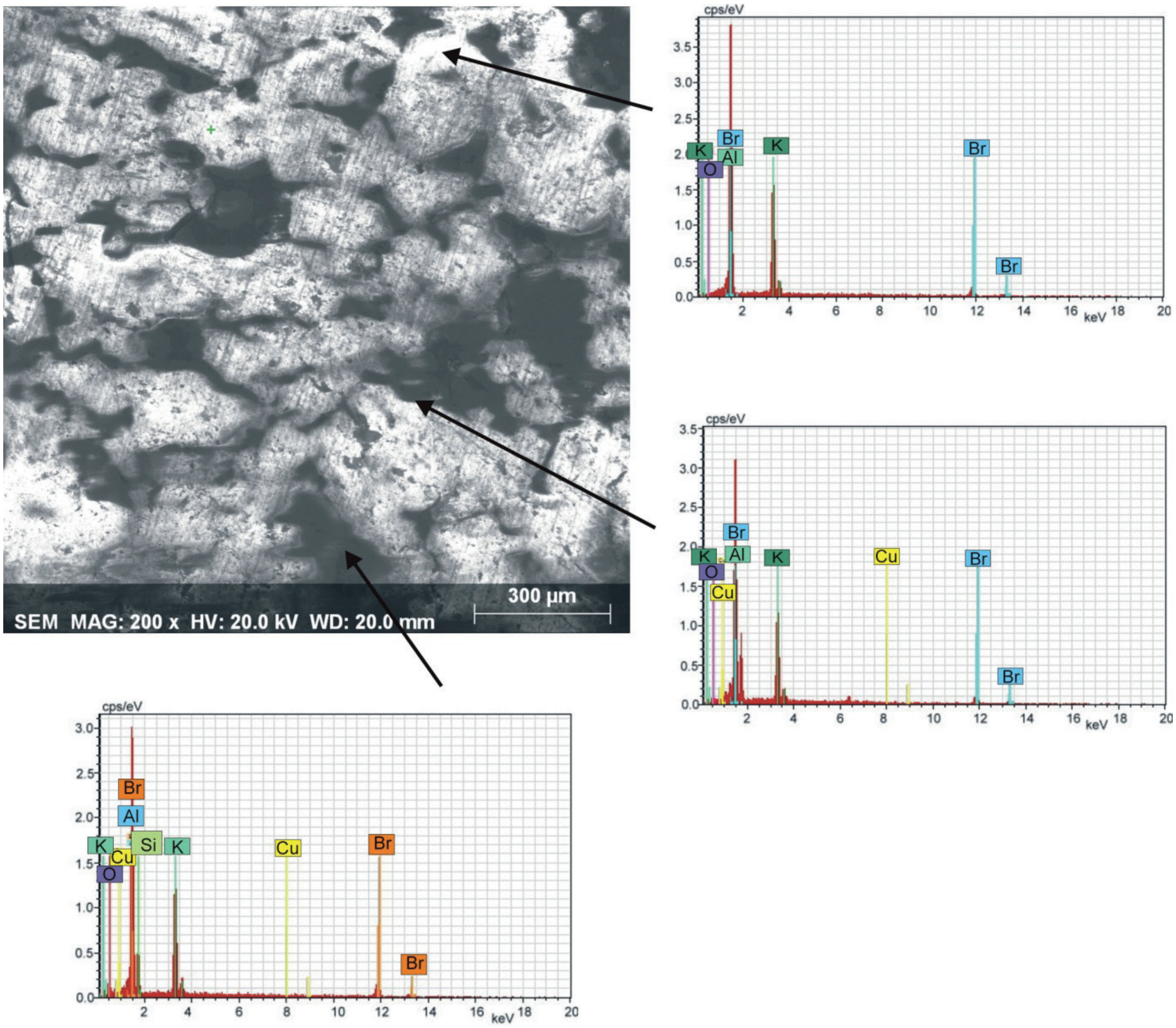

Fig. 9. SEM micrograph and EDS spectrum of elements in waste foundry molding sand after adsorption process

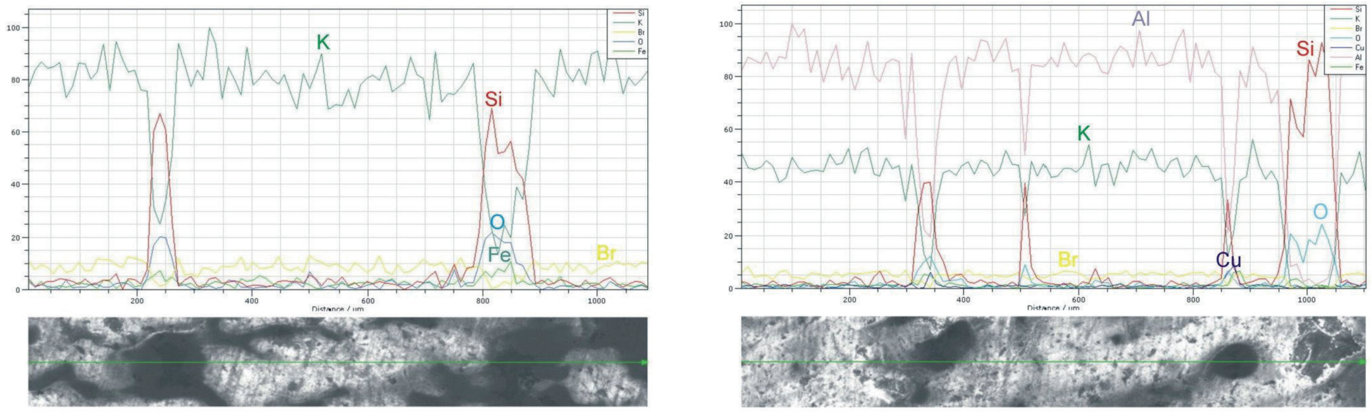

Fig 10 a

Fig 10 b

Fig. 10. EDS line analysis of waste foundry molding sand: a) before the adsorption process, b) after adsorption process

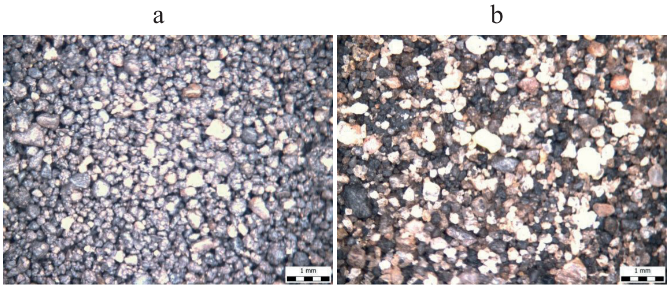

Fig. 7. Light micrograph of waste foundry molding sand before adsorption process (a) and after adsorption process (b)

Figure 7a shows that the clay bonded waste foundry molding sand before adsorption process is much homogenous with uniform grains size. In Figure 7b, which is taken after adsorption process, dark grains are clearly visible, indicating an adsorbed Cu (II) ions on waste foundry molding sand.

Average grains sizes determined from micrographs showed in Figure 7 are given in Table 5.

TABLE 5
Grain size of samples according to ASTM E112-96

Sample	Diameter, μm	G	% of removal
Waste foundry molding sand	203,26	1,64	-
Waste foundry molding sand +Cu(II)	222,41	1,38	72,94

TABLE 6
Adsorption capacities of Cu (II) ions on different low-cost adsorbents

Adsorbents	Adsorption capacity (mg/g)	Literature
Walnut Shell	0.106	[26]
Steel making slag	6.2	[27]
Sugar beet pulp	0.15	[28]
Citric acid modified soybean hulls	154.9	[29]
Carrot residue	32.74	[30]
Activated carbon	5.0	[31]
Waste foundry sand	3.31	[25]
Rhizopus arrhizus	33.8	[32]
Oyster shell	3.05	[33]

These results show the increase of average diameter of grains in microstructure due to adsorption Cu (II) ions. Namely, after adsorption of Cu (II) ions, diameter of grains was increased for 9.42 %. This increased value indicates that adsorption of Cu (II) really occurred.

These results are confirmed by calculating the percentage of removal Cu (II) ions from solution (Table 5). This percentage is relatively high, indicating very good adsorption characteristics of sample.

For the further detail investigation of microstructure, scanning electron microscope with energy-dispersive spectrometer was used. SEM micrograph of clay bonded waste foundry molding sand (Figure 8) shows three characteristics fields: gray in majority, dark and white field. According to the EDS results, the gray field presents clay bonded waste foundry molding sand (as a complete mixture) containing foreign metal particles (Fe, Mn) which probably originate from the removal of final castings from mold and oxidation of melting alloy during the casting process. Dark filed presents grains of silica sand (SiO2), while white field is KBr which served as binder. After adsorption process peaks for copper were visible on the edges of matrix (Figure 9). All of the above is confirmed by line analysis (Figure 10).

Results of EDS line analysis of waste foundry molding sand before the adsorption process (Figure 10a) show that in the dark field exist an oxide of silicone originate from the sand and an oxide of iron originate from oxidation during the casting process. White areas include bind for preparing discs of sample i.e. KBr. After adsorption process in the microstructure of investigated sample characteristic peaks of Cu (II) ions were obvious (Figure 10b) confirming the bonding of these ions from the solution, i.e. adsorption process.

Literature data show that the adsorption of Cu (II) ions is possible on other waste materials. Table 6 shows adsorption capacities of Cu (II) ions on different low-cost adsorbents.

4. Conclusion

Obtained results indicate that the waste foundry molding sand can be used as inexpensive adsorbent for the removal of Cu (II) ions from aqueous solutions. Coefficients of determination for Freundlich and Langmuir isotherms indicate the possibility of the chemical and physical adsorption of Cu (II) ions on the waste foundry molding sand. However, it is more likely that the adsorption takes place as chemisorption, since obtained coefficients of determination indicate that the adsorption of Cu (II) ions on the waste foundry molding sand takes place according to the reactions of pseudo second order. The results of thermodynamic analysis also indicate on chemisorption. Microscopic analysis supports all these claims.

REFERENCES

[1] J. Jorstad, M.B. Krusiak, J.O. Serra, V.L. Fay, Aggregates and Binders for Expendable Molds, chapter in ASM Handbook Casting, ASM International, Materials Park, Ohio, **15**, 528 - 548 (2008).

[2] R. Siddique, Waste Materials and By-Products in Concrete, Springer, 2008.

[3] R.S. Dungan, N.H. Dees, J. Environ. Manage. **90**, 539-548 (2009).

[4] G. Singh, R. Siddique, Constr Build Mater. **26**, 416–422 (2012).

[5] A. Štrkalj, A. Rađenovć, J. Malina, Arch. Metall. Mater. **55** (2), 449-454 (2010).

[6] I. Šipuš, A. Štrkalj, Z. Glavaš, Can Metall Quart. **51**, 13-18 (2014).

[7] E.H. Gürkan, S. Çoruh, C. Kılıcoglu, Journal of Selçuk University Natural and Applied Science, Special Issues ICOEST. **2**, 289-298 (2014).

[8] I. Campos, J.A. Álvarez, P. Villar, A. Pascual, L. Herrero, Environ. Technol. **34**, 1267 – 1281 (2013).

[9] E.H Gurkan, S. Çoruh, Environ. Eng. Manage. J. (Papers accepted for publication)

[10] S. Çoruh, E.H. Gurkan, Environ. Prog. Sustain. Energy. **33**, 1086-1095, (2014).

[11] A. Strkalj, Z. Glavas, I. Brnardic, Chem. Biochem. Eng. Q. **27**, 15-19 (2013).

[12] A. Strkalj, Z. Glavas, K. Maldini, Inženjerstvo okoliša. **1**, 77-79 (2014).

[13] A. Strkalj, Z. Glavas, K. Maldini, LJ. Slokar, D. Hrsak, Machines, Technologies, Materials **4**, 12-14 (2015).

[14] T. Lee, J. Park, J. Lee, Chemosphere. **56**, 571-581(2004).

[15] B.R. Stern, M. Solioz, D. Krewski, P. Aggett, T. Aw, S. Baker, K. Crump, M. Dourson, L. Haber, R. Hertzberg, C. Keen, B. Meek, L. Rudenko, R. Schoeny, W. Slob, T. Starr, J. Toxicol. Environ. Health Part B **10**, 157–222 (2007).

[16] Narodne novine (2013): Pravilnik o graničnim vrijednostima emisija otpadnih voda NN 80/2013.

[17] A.O. Dada, A.P. Olalekan, A.M. Olatunya and O. Dada, IOSR J Appl Chem. **3**, 38-45 (2012).

[18] L.M. Peruchi, A.H. Fostier, S. Rath, Chemosphere. **119**, 310–317 (2015).

[19] S. Goldberg, Equations and Models Describing Adsorption Processes in Soils, Soil Science Society of America, Road, Madison, Chemical Processes in Soils, 2005.

[20] J. Kim, S. Xu, Chemosphere **144**, 555–563 (2016).

[21] G.Vijayakumar, R.Tamilarasan, M. Dharmendirakumar, J Mater Environ Sci. **3**, 157-170 (2012).

[22] D.D. Duong, Adsorption analysis: equilibria and kinetics, Imperial College Press, London, 1998.

[23] S. Hong, C. Wen, J. He, F. Gan, Y.Ho, J Hazard Mater. 167, 630–633 (2009).

[24] Z. Bekci, Y. Seki, M. K. Yurdakoc, J. Mol. Struct. 827, 67–74 (2007).

[25] E.H. Gürkan1, S. Çoruh, C. Kılıçoğlu, Journal of Selçuk University Natural and Applied Science. 1, 289-298 (2014).

[26] T. Altun, E. Pehlivan, Clean. **35**(6), 601 – 606 (2007).

[27] D. H. Kim, M. Shin, H. Choi, C. Seo, K. Baek, Desalination **223**, 283–289 (2008).

[28] E. Pehlivan, S. Cetin. BH. Yanik, J. Hazard. Mater. **135**, 193-199 (2006).

[29] W.E Marshall L.H. Wartelle, D.E. Boler, M.M. Johns, C.A. Toles, Bioresour. Technol. **69**, 263–268 (1999).

[30] B. Nasernejad, T.E. Zadeh, B.B. Pour, M.E. Bygi, A. Zamani, Process Biochem. **40**, 1319-1322 (2005).

[31] E. Pehlivan, G. Arslan, Energy Sources. **28**A, 1099-1112 (2006).

[32] Y. Sağ, A. Kaya, T. Kutsal Hydrometallurgy **50**, 297-314 (1998).

[33] Q. Wu, J. Chen, M. Clark , Y. Yu, Appl Surf Sci. **311**, 264–272 (2014).