Acta Technica 61, No. 4B/2016, 307–314

Sorption properties of carbon waste pyrolysis product for biological wastewater treatment

Ilnar A. Nasyrov[1], Stanislav V. Dvoryak[2], Ildar G. Shaikhiev[3]

Abstract. Influence of pH, temperature and time of contact for adsorption of heavy metals are studied. Experiments on model solutions of heavy metals ions at 20 °C against constant pH value are provided. From the obtained data, isotherms of sorption are constructed and sorption size is calculated. Dependence of sorption extent of heavy-metal ions on volume of the past model solution is studied. Also, the influence of temperature and time on the sorption of heavy-metal ions is investigated. It is found that the adsorption time is 15 minutes for copper ions and 10 minutes for the iron and chromium ions. When the temperature rises to 60 °C, the time of sorption of heavy-metal ions is reduced insignificantly (on 5–10 min). According to the obtained results, the maximum degree of adsorption on iron ions (III) was 95.9 %. After passing through the sorbent model solution obtained in 4 dm^3 volume, the degree of adsorption decreased to 50.9 %.

Key words. Silt rainfall, pyrolysis, sorbent, waste, heavy-metal ions.

1. Introduction

Urban agglomeration with domestic and industrial human activities generate liquid waste in the form of wastewater that is taken off into the sewer. Purification of domestic and industrial wastewater is an urgent problem for urban areas. Sewage treatment plants come on, performing cleaning stages. Steps of wastewater treatment are traditional and include the following main operations [1]: mechanical wastewater treatment in primary sedimentation tanks, biological treatment in aeration tanks, cleaning of suspended solids of activated sludge in secondary sedimentation tanks, advanced treatment of water, and disinfection. During the passage of wastewater through the purification steps in treatment plants, there is formed sludge sediment in the majority, not amenable to any processing except dewatering sludge

[1]Federal University, Naberezhnye Chelny, Prospect Mira 68/19, Russia, 423810
[2]Lomonosov Moscow State University, Moscow, Leninskiye Gory, GSP-1, Russia, 119899
[3]Kazan National Research Technological University, Kazan, Karl Marx street 68, Russia, 420015

on fields in vivo [2]. This process takes a long term and large areas under sludge. Also, storage of silt rainfall leads to the spread of negative gas background and does not preclude the pollution of soil, surface water and groundwater, vegetation by toxic components that are part of rainfall. Russian Federation annually produces more than 2 million tons of sewage sludge regarding dry matter [3]. Large amounts of sediment, multicomponent, and the presence of their composition in heavy metal compounds, along with other pollutants, as well as the lack of appropriate recycling technologies lead to their accumulation and, consequently, the rejection of land for storage. Existing methods for recovery and recycling of deposits of biological wastewater suggested in the past as a source for producing activated carbon 4–6, complex sorption materials intended to remove heavy-metal ions, bioremediation of oil-contaminated soil, and use of sewage sludge as fertilizer. Application of sewage sludge to produce activated carbon was advantageous due to the high carbon content in the dry matter of sludge and low mass loss during the carbonization. During pyrolysis, a solid residue - Pyro Carbon is produced or its mineral compositions. Research has shown that the pyrolysis product is an available sorption material, the cost of which is much lower than that of industrial sorbents. The most expedient use of the resulting material as a sorbent is at a local emergency spills of oil and oil products, as well as for deep purification of sewage, and biological treatment of the past. Organic and mineral composition can be used for remediation and detoxification of waste sludge and canned cards. Introduction of them to the sludge storage area will contribute to the structuring of processes and humification of the emerging soils. The pyrolysis of sewage sludge with precipitation fields at 775–825 °C allows obtaining activated carbon with a high specific surface area and microporosity. Note that during the carbonization of dry matter of sewage sludge, the maximum amount of volatile compounds is distilled at 265–330 °C, and the carbonized precipitate is formed, when temperature without air access reaches 420–655 °C. Recycling sludge in this way allows getting rid of the sludge pit and improving the quality of wastewater.

2. Experimental part

To determine the optimum pH range in a series of conical flasks, 1 g of sorbent, and 250 ml of model solution corresponding heavy metal ion at a concentration of 1–50 mg/dm^3 were taken, (the pH factor being adjusted from 2 to 12), capped and mixed in a shaker for 2 hours under thermostatic control (20±0.1 °C). Next, the filtrate was separated from the sorbent and we determined the initial and final concentration of heavy metals ions by atomic absorption spectroscopy with a spectrometer marks "QUANT-Z". Sorption time varied between 10 and 120 minutes. The concentration of heavy metal ions was 1–50 mg/dm^3. When studying the effect of temperature on the degree of extraction, it ranged from 20 to 60 °C. At the end of each experiment, the degree of sorption was calculated. The data obtained were used to construct graphs "the degree of sorption - time" that make possible to determine the optimal time needed to achieve the maximum degree of sorption. To obtain sorption isotherms in series conical flasks, we used 1 g of sludge pyrolysis product, added 250 ml of a solution containing heavy metal ions with concentrations in the range 1 to 2000 mg/dm^3, capped and stirred in a shaker. It was found that at this ratio and weight linkage metal concentration in the solution, there was reached equilibrium 15 minutes after the start of the experiment [7]. The solution was then separated from the sorbent and its concentration was determined in the investigated metal.

3. Results and discussion

In this paper, we studied the particle size, structure and elemental composition of activated carbon sorbent, see Fig. 1. Then we investigate the sorption properties of carbon sorbent in static conditions. The study results indicate that the sorbent has a porous structure with a grain size of 200–500 microns, preferably rectangular. The porous structure allows predicting the sorption properties of carbon sorbent obtained by pyrolysis of the sludge. The results of the study of the elemental composition of the resulting carbon sorbent are shown in Table 1.

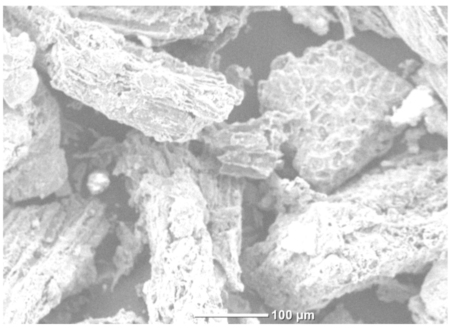

Fig. 1. Activated carbon sorbent received as a result pyrolysis of silt rainfall

The high content of organic compounds in the dry matter of the silt rainfall leads to the total content of carbon and oxygen higher than 86 % of the elemental composition of the analyzed sorption material. The mineral part of carbon sorbent accounts for less than 14 % of the elemental composition. A laser particle size analyzer brand "Microsizer 201C" defined particle size distribution. According to a granulometric analysis of sorbent it consists of 34.1 % of particles with sizes ranging from 200 to 300 microns, 59.8 % of particles with sizes from 300 to 600 microns and 3.1 % of particles with sizes from 10 to 200 microns. Later we determined sorption characteristics of the resulting product of the pyrolysis of silt rainfall. Figure 2 depicts the percentage of heavy metals including Fe (III), Cu (II) and Cr (VI) in various concentration.

Table 1. Elemental composition of carbon sorbent

Element	C	O	Ca	Fe	Si	P	Al	K	Na	Mg	S
Mass fraction (%)	59.18	26.87	4.02	2.83	2.44	1.78	1.27	0.48	0.18	0.53	0.42

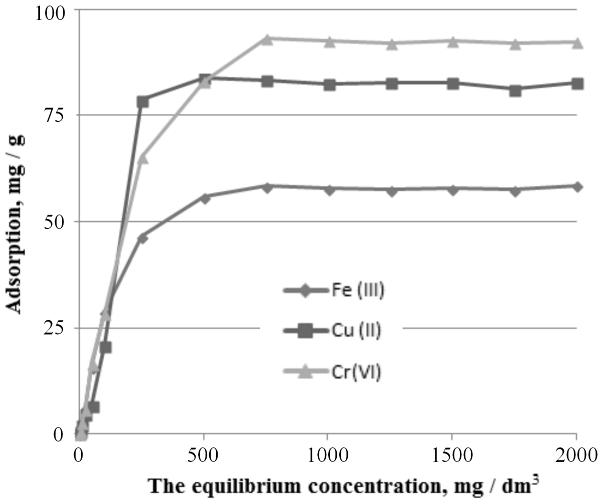

Fig. 2. Adsorption isotherms of iron ion, copper and chromium on obtained sorbent

Based on the values of calculated sorption value (a, (mg/g)) according to the formula [7]

$$a = \frac{(C_0 - C_1) \cdot V}{m_c}, \tag{1}$$

where V is the solution volume (cm^3 and m_c is the sorbent mass (g), we can draw the dependencies of the adsorption on the equilibrium concentration. Experiments were carried out on the model solutions at 20 °C with the constant value of pH. Data for the analysis of the isotherms in Fig. 2 give grounds to assert that the saturation point of the projection on the y-axis indicates the magnitude of the sorption capacity of carbon sorbent on heavy metal ions [8]. It was determined that the maximum adsorption capacity for Cu_2^+ ions is 84 mg/g, for Fe_3^+ ions it is 59 mg/g, and for Cr_6^+ ions it is 93 mg/g. For comparison, Table 2 shows the adsorption capacity of activated carbon (BAU-A) and activated carbon fiber before treatment (AYV) and after treatment with nitric and sulfuric acids (OAYV-sulfuric and OAYV-nitric) [9].

Table 2. Sorption characteristics of carbon adsorbents

Adsorbent	Conductivity adsorption (mg/g)		
	$Cr_2O_7^{2-}$	Fe^{3+}	Cu^{2+}
BAU-A	28.0		3.3
AYV	36.0		12.2
OAYV-sulfuric	37.2	13.5	12.7
OAYV-nitric	42.0	10.2	16.6

According to the classification [10], the obtained isotherm belong to class L (Langmuir isotherms), L-2 type. This type of isotherms (L) is characterized by the independence of the heat of adsorption on the surface coverage and the lack of competition from the solvent. With the increase in the employment share of adsorption sites, adsorptive molecules can with more difficulty find a vacant place, especially if they are prone to the formation of large associates to increase their concentration in the solution due to the intermolecular interaction. L-2 type isotherm characteristic at a certain concentration reaches the saturation adsorption of the adsorptive. Table 3 shows the Langmuir equation constants (K_{L}) for the adsorption of iron ions, copper, and chromium on pyrolysis of the silt rainfall product.

Table 3. Parameters of Langmuir equation for sorption of heavy metal ions on sorption material

heavy metal ions	a_m (mg/g)	$K_{\mathrm{L}} \cdot 10^{-3}$
Fe^{3+}	58.6	1.39
Cu^{2+}	83.8	1.90
Cr^{6+}	93.0	2.62

To select the optimal conditions for the sorption, we carried out studies of the sorption characteristics of carbon sorbent in the static mode, determined by the effect of pH, temperature, and time on the processes of sorption by ions heavy metal. Figure 3 illustrates the effects of pH percentage on absorption of heavy metals.

The degree of adsorption (R (%)) was calculated by the formula

$$R = \frac{C_0 - C_1}{C_0} \cdot 100\,, \tag{2}$$

where C_0 is the initial concentration, (mg/dm^3) and C_1 is the concentration of heavy metal ions (mg/dm^3) after sorption.

Based on the results of the experiment we plotted graphs $R = f(\mathrm{pH})$ and determined the region of optimal acidity values in them, in which the adsorption of heavy metal ions is maximized. The value R for every such point was taken as the average of three independent parallel experiments. The results showed the greatest degree of sorption of heavy metal ions observed for pH ranging from 6 to 12. Increasing the effectiveness of purifying at pH>8 indicates the precipitation of metal hydroxides

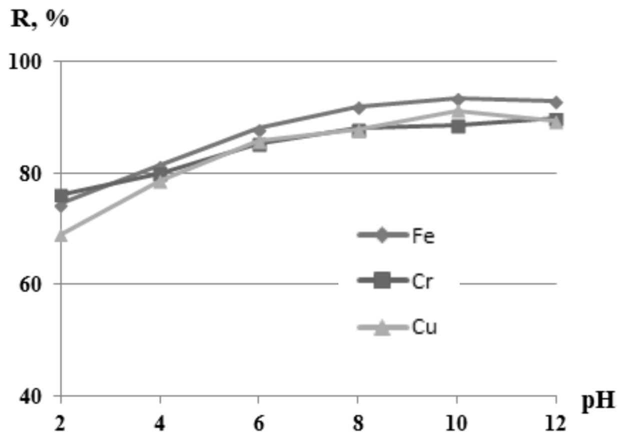

Fig. 3. Effect of pH on sorption of heavy-metal ions

and the flow of reagent purification. In the adsorption process it is influenced by factors such as time and temperature. The graphic dependence of the degree of sorption of heavy metal ions on the phase contact time at various temperatures in a neutral medium is shown in Fig. 4.

Studies of the kinetics of adsorption of heavy metal ions indicate that coal sorbent obtained by pyrolysis of the silt rainfall is characterized by a relatively high speed of the process. By evaluating the absorption time of ions by high ratios at initial times, it is found that the adsorption time is 15 minutes for copper ions and 10 minutes for the iron and chromium ions. When the temperature rises to 60 °C during the sorption of heavy metal ions, this time is reduced insignificantly (to 5–10 minutes). Increased temperature also results in a slight increase in the degree of adsorption (not more than 5 %). In an acid medium (pH < 3) we get similar results, but with a lower extent of sorption ($R(\mathrm{Cr}^{6+}) = 82\,\%$; $R(\mathrm{Cu}^{2+}) = 77\,\%$; $R(\mathrm{Fe}^{3+}) = 86\,\%$). Subsequently, experiments were conducted to study the carbon sorbent sorption parameters on iron ions in dynamic conditions. For this purpose, to a series of glass columns of height 150 mm and diameter 10 mm there was placed 1.5 g of the reagent and model solution proceeded with a concentration of iron ion (III) 5 mg/dm^3.

4. Conclusion

According to the obtained results, the maximum degree of adsorption on iron ions (III) was 95.9 %. After passing through the sorbent model solution obtained in 4 dm^3 volume, the degree of adsorption decreased to 50.9 %. Therefore, it is shown that the method of recycling of deposits of biological sewage treatment by pyrolysis provides a comprehensive sorption material. Studies of the structure and sorption properties showed the possibility of using silt rainfall pyrolysis product as a sorption material for the removal of heavy metal ions from aqueous media.

*** March 8, 2017 ***

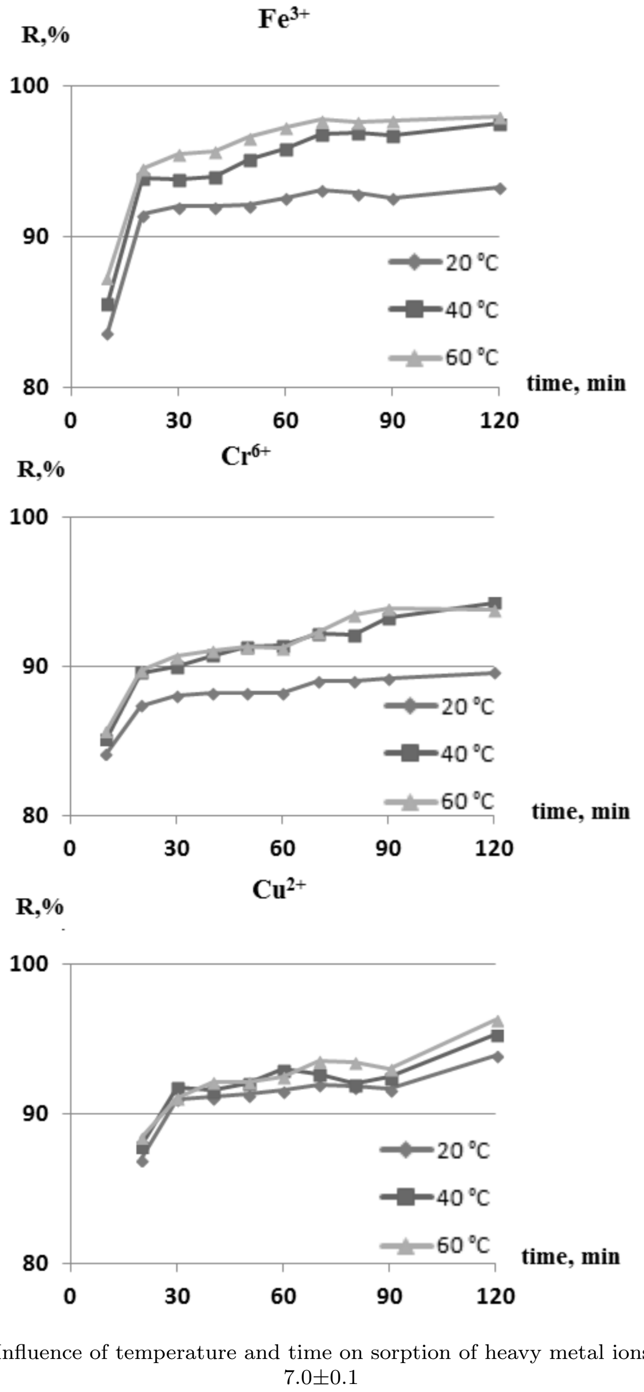

Fig. 4. Influence of temperature and time on sorption of heavy metal ions (pH = 7.0 ± 0.1

References

[1] S. M. Seyedhosseini, M. J. Esfahani, M. Ghaffari: *A novel hybrid algorithm based on a harmony search and artificial bee colony for solving a portfolio optimization problem using a mean-semi variance approach.* J Central South University *23* (2016), No. 1, 181–188.

[2] Y. Pourasad, M. Mahmoodi-k, M. Oveisi: *Design of an optimal active stabilizer mechanism for enhancing vehicle rolling resistance.* J Central South University *23* (2016), No. 25, 1142–1151.

[3] C. Palanichamy: *A sustainable energy option to the expanding chennai metropolitan area.* Indian Journal of Science and Technology *8* (2015), No. 22.

[4] B. Mashadi, M. Mahmoodi, A. H. Kakaee, R. Hosseini: *Vehicle path following control in the presence of driver inputs.* Proc. Institution of Mechanical Engineers, Part K: J Multi-body Dynamics *227* (2013), No. 2, 115–132.

[5] R. R. Zinnatov, G. V. Mavrin, I. A. Nasyrov, M. P. Sokolov, D. A. Kharlyamov: *Sorption concentration of ions of copper (II) and lead (II) by magnetic sorbent.* Research Journal of Pharmaceutical, Biological and Chemical Sciences *6* (2015), No. 5, 1623–1628.

[6] G. H. Yunusa, A. Kassim, N. Gofar: *Effect of surface flux boundary conditions on transient suction distribution in homogeneous slope.* Indian Journal of Science and Technology *7* (2014) No. 12, 2064–2075.

[7] D. A. Kharlyamov, G. V. Mavrin, I. Y. Sippel: *About the possibility of sorption concentration of heavy metals using magnetite.* Life Science Journal *11* (2014), No. 8, 607–610.

[8] D. A. Kharlyamov, G. V. Mavrin, E. A. Danilova, R. R. Zinnatov, E. V. Prytkova, S. V. Dvoryak: *Application of a magnetic composite sorbent on the basis of woodworking waste for sewage treatment from heavy metals.* Research Journal of Pharmaceutical, Biological and Chemical Sciences *7* (2016), No. 3, 1667–1670.

[9] G. Singh, A. Perwez: *Estimation of assimilative capacity of the airshed in iron ore mining region of goa.* Indian Journal of Science and Technology *8* (2015), No. 23.

[10] G. Parfit, K. Rochester: *Adsorption from solutions on solid surfaces: Translation from English.* Publishing house Mir, Moscow, Russian. (1986).

Received November 16, 2016