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THE POST-TREATMENT OF GALVANIC WASTEWATER FROM CHROMIUM (VI), COPPER (II) AND NICKEL (II) IONS USING MAGNETIC COMPOSITE MATERIALS

D. A. Kharliamov*, D. A. Albutova, S. R. Gafiiatova, G. V. Mavrin

Kazan Federal University, Naberezhnye Chelny Institute

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ABSTRACT

The possibility of post-treatment of galvanic wastewater containing Cr^{6+}, Cu^{2+} and Ni^{2+} ions by the sorption method was studied. As sorption materials the MDF waste wood fiber and activated carbon BAU-A were used. To improve the sorption characteristics, magnetite was deposited on the surface of the considered materials, which resulted in the production of composite materials with magnetic properties. The factors affecting the sorption properties of the samples were analyzed in the static mode: the temperature and contact time of the phases. The calculation of the thermodynamic parameters of the sorption process (reaction order, Gibbs energy, entropy, enthalpy, activation energy) is given, during which a mixed mechanism of the adsorption process was revealed. Comparative studies of the sorption properties of modified waste wood fiber and activated carbon with their untreated analogs were carried out under dynamic conditions. According to the conducted studies, the maximum dynamic exchange capacity for a modified wood fiber sample was 5.92 mg/g for Cr^{6+}, 5.03 mg/g for Cu^{2+}, and 3.61 mg/g for Ni^{2+}, which is superior to sorption both untreated waste wood fiber and a well-known industrial sorbent – activated carbon BAU-A. This circumstance is due to the presence of magnetite in the composition of modified samples of wood fiber and activated carbon, which contributes to an increase in sorption capacity. It is established that the obtaining of these sorption materials is expedient both in the ecological and in economic terms because of the ease of production, low cost, good sorption properties, and the possibility of disposing secondary raw materials.

Keywords: waste wood fiber, activated carbon, magnetite, sorption, heavy metals.

Author Correspondence, e-mail: kharlyamov@gmail.ru

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INTRODUCTION

Galvanic production has been widely developed in the territory of our country. At present, a significant amount of wastewater containing heavy metal ions is discharged into the environment by various enterprises engaged in metal etching and galvanic coating. Technologies the most enterprises use do not provide effective removal of heavy metal ions, and their content in sewage in many cases exceeds the permissible levels. After the reagent treatment, which is often used in industry, the residual content of heavy metal ions reaches 1-10 mg/dm^3, with the norm for most metals being 0.05-1 mg/dm^3. The above circumstances require the use of additional methods to reduce the residual concentration of heavy metal ions [1].

Most of the currently used methods for treatment of galvanic wastewater, such as flocculation, coagulation, cementation, chemical precipitation, electrochemical methods, are most effective in purifying highly concentrated effluents, allowing most of the pollutants contained in the aqueous phase to be extracted from the aqueous phase [2]. However, the degree of extraction of heavy metal ions obtained is, as a rule, not high enough. A number of methods such as ion exchange, liquid extraction, ultrafiltration and reverse osmosis [3] make it possible to achieve a deep degree of purification from heavy metal ions, however, they are usually unsuitable for the processing of highly concentrated effluents due to the cyclic nature of the instrumentation schemes of purification processes and low productivity of a single cycle. In addition, most of the methods listed are oriented towards the use of expensive imported equipment and consumables. In the current situation in the state economy, searching for new inexpensive materials highly efficient and cost-effective in sewage treatment is relevant. Of particular interest in this case are sorption materials from waste products containing cellulose in their composition. Large reserves, low cost, renewable raw materials base, the possibility of utilization determine the practical and economic feasibility of using the latter for wastewater treatment [4-6].

Based on the foregoing, the objective of this research was to improve the efficiency of galvanic production waste water treatment from Cr^{6+}, Cu^{2+} and Ni^{2+} ions using magnetic composite sorbents based on waste wood fiber (*WWF*) from MDF boards, activated carbon (*BAU-A*) and magnetite (Fe_3O_4) having sorption capacity in relation to ions of heavy metals [7]. The advantage of such sorption materials is that during the contact wastewater treatment the use of sorbents with magnetic properties greatly simplifies the adsorption process due to fast sorption and ease of separating the sorbent from solutions by magnetic separation [7-8].

In the course of the research, the factors influencing the sorption properties of the samples were analyzed such as the temperature and time of phase contact; the thermodynamic parameters of the sorption process were calculated; the dynamic and total exchange capacity with respect to Cr^{6+}, Cu^{2+} and Ni^{2+} ions were calculated; a dose of sorbents for post-treatment of galvanic wastewater was calculated.

MATERIALS AND METHODS

To obtain sorption materials on the surface of waste wood fiber and coal, the magnetite particles were precipitated. Precipitation was carried out from a solution containing a mixture of ferric chloride and ferrous chloride under the influence of ultrasonic oscillations at a frequency of 35 kHz (t=15 min, I=450 W/cm^2) at 25±5 °C with ammonia water in the following mass ratios of the components: $FeCl_3$ – $FeCl_2$ 10:2.23:0.99. The resulting products were repeatedly washed with water until neutral, and then dried at 110 °C for 2 hours.

In the course of the research, the change in the sorption capacity of the sorption materials based on the time of contact was studied. To this end, a 0.1 dm^3 solution containing Cr^{6+}, Cu^{2+} and Ni^{2+} ions with a concentration of 10 mg/dm^3 was poured into a series of flasks, then a sample of sorption material with a mass of 0.1 g was placed in each vessel. The contents of the flasks were stirred on a shaker for a predetermined time interval. The content of heavy metal ions was measured with the Agilent 720 ICP-OES atomic emission spectrometer in accordance with the procedure [9]. The experiments were carried out at temperatures of 278, 293, 313 and 333 K. The residual content of heavy metal ions in the samples was determined at definite intervals after the start of the experiment. To calculate the static exchange capacity (*SEC*), the following formula was used:

$$SEC = \frac{(C_0 - C_1)\cdot V}{m}, \quad (1)$$

Where V – the volume of the solution poured to the sorbent, dm^3; C_1 – equilibrium concentration of ions of heavy metals in solution, mg/dm^3; C_0 – the initial concentration of heavy metal ions in solution, mg/dm^3, m – sorbent weight, g.

The process of sorption of Cr^{6+}, Cu^{2+} and Ni^{2+} ions under dynamic conditions was carried out according to the method [10]. Experimental studies were carried out in a glass column of 15 mm in diameter, filled with sorption materials in an amount of 5 g (size fractions 0.5-3 mm). The solution was continuously passed through the adsorbent bed from top to bottom until the adsorbent was completely saturated with the adsorbed material. The initial concentration of heavy metal ions in the solution is 10 mg/dm^3, the sorption volume is 10 cm^3, the filtration rate is 10 m/hour.

Based on the results of the experiment, a dynamic exchange capacity (*DEC*) was calculated that characterizes the capacity of the sorbent prior to the onset of the “slip" of the adsorbed ions:

$$DEC = \frac{1}{m}\sum_{C=0}^{C=0,05C0}\left[V_1(C_0 - C\ )\right], (2)$$

where C – the concentration of heavy metal ions at the outlet of the column, mg/dm^3, V_1 – the portion of the filtrate with concentration C, dm^3.

The experiments on the simulation of the removal of heavy metal ions used waste water from the electroplating shop, pre-cleaned by a reagent method. The minimum dose of the sorbent for post-treatment of galvanic wastewater was determined according to the following formula:

$$D_{\min} = \frac{C_0 - C_2}{K \cdot CEC}, (3)$$

where C_2 – the residual concentration in the filtrate, mg/dm^3; K – the coefficient of exhaustion of the sorbent capacity, assumed equal to 0.7.

RESULTS AND DISCUSSION

As an initial material for the production of sorption materials, waste wood fiber from MDF boards, formed in a wood processing plant, and activated birch charcoal were used. The considered enterprise produces MDF-plates mainly from softwood (aspen, birch, linden). Waste wood fiber is formed during the formation of fibers in the production cycle of MDF products and is reject that is unsuitable for further use in production [8]. For the experiments, an average sample was taken from the entire site of temporary waste storage.

In the course of the research, the change in the sorption capacity of the modified and initial samples based on the time of contact was studied. Fig. 2 shows the dependence of the sorption capacity of sorption materials on time at a temperature of 294 K.

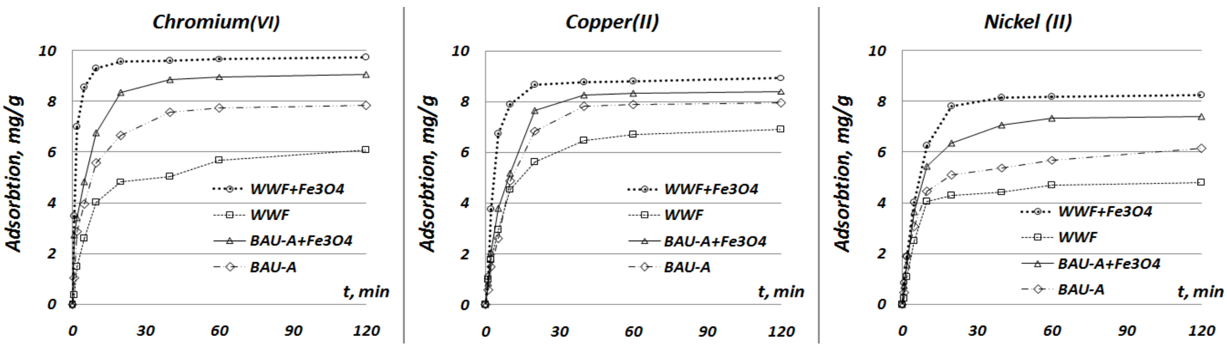

Fig.2. Dependence of the sorption capacity of the samples from time (T=294 K)

As we can see from the graphical dependences, the sorption capacity of the samples increases with increase in the time of contact. The maximum values of the static exchange capacity are observed in magnetic composite sorbents and are 9.66 mg/g of Cr^{6+}, 8.79 mg/g of Cu^{2+}, 8.10 mg/g of Ni^{2+} ions for WWF+Fe_3O_4, and 8.97 mg/g of Cr^{6+}, 8.10 mg/g of Cu^{2+}, and 7.03 mg/g of Ni^{2+} ions for BAU-A+Fe_3O_4. For unmodified samples, the values of the static exchange capacity are much lower and make up Cr^{6+} – 5.60 mg/g, Cu^{2+} – 6.68 mg/g, Ni^{2+} – 4.56 mg/g for wood fiber, and Cr^{6+} – 7.72 mg/g, Cu^{2+} – 7.86 mg/g, Ni^{2+} – 5.58 mg/g for activated carbon.

In the case of experiments conducted at temperatures of 314 and 334 K, analogous dependences of the sorption capacity increase on increasing temperature and phase contact time were revealed for modified sorption materials. The maximum values of the sorption capacity are observed at a temperature of 334 K for the WWF+Fe_3O_4 andBAU-A+Fe_3O_4 samples and exceed the values of the sorption capacity of unmodified samples.

It was established that the experimental data are correctly described by a pseudo-second-order model, implying that the chemical interaction stage is the limiting one. This circumstance explains the fact that adsorption proceeds rapidly at the initial stage and slows down when approaching the equilibrium state, and with increasing temperature the rate of the sorption process increases, while the time for achieving equilibrium decreases [11]. Thus, we can conclude that the sorption process is controlled by both internal and external diffusion. According to the calculations, it is determined that the minimum time for the onset of equilibrium for samples of magnetic composite sorbents is 10-12 minutes at a temperature of 334 K.

During the processing of the kinetic curves, the reaction rate constants (k_2) were calculated, the thermodynamic parameters such as (enthalpy (ΔH), entropy (ΔS), Gibbs energy (ΔG), and activation energy (E_a) were defined for determining the possible mechanisms of the process, its heat effect and character (Table 3).

Table 3. Kinetic and thermodynamic parameters of sorption of heavy metal ions by magnetic composite sorbents

Sample	***Ion***	***T, K***	***k_2, $g \cdot mg^{-1} \cdot min^{-1}$***	***ΔH, $kJ \cdot mol^{-1}$***	***ΔS, $kJ \cdot mol^{-1} \cdot K^{-1}$***	***ΔG, kJ***	***E_a, $kJ \cdot mol^{-1}$***
WWF+Fe_3O_4	Cr^{6+}	294	0.082	7.15	0.0429	-5.46	18.49
		314	0.095		0.0428	-6.30	
		334	0.106		0.0427	-7.12	
	Cu^{2+}	294	0.103	4.89	0.0385	-6.43	14.27
		314	0.159		0.0384	-7.16	
		334	0.244		0.0382	-7.88	
	Ni^{2+}	294	0.123	7.24	0.0335	-2.59	11.88
		314	0.202		0.0331	-3.16	
		334	0.395		0.0330	-3.77	
BAU-A+Fe_3O_4	Cr^{6+}	294	0.101	6.41	0.0409	-5.60	16.89
		314	0.119		0.0402	-6.22	
		334	0.127		0.0399	-6.93	
	Cu^{2+}	294	0.115	4.75	0.0363	-5.91	13.30
		314	0.186		0.0361	-6.59	
		334	0.271		0.0359	-7.25	
	Ni^{2+}	294	0.145	6.94	0.0321	-2.48	10.90
		314	0.232		0.0318	-3.05	
		334	0.427		0.0317	-3.64	

Based on the obtained data, the possibility of sorption progress increases along with increasing temperature, which in turn indicates the endothermic nature of the process. The obtained values of activation energy and positive values of enthalpy confirm that chemisorption is the limiting stage. This circumstance is presumably due to the presence of magnetite and cellulose, hydroxyl, carbonyl and carboxyl groups in the composition, which was confirmed by previous experiments [7].

The next stage of the study was the dynamic testing of magnetic sorption materials. Fig. 3 shows the output curves of sorption of heavy metal ions at a rate of 10 m/h.

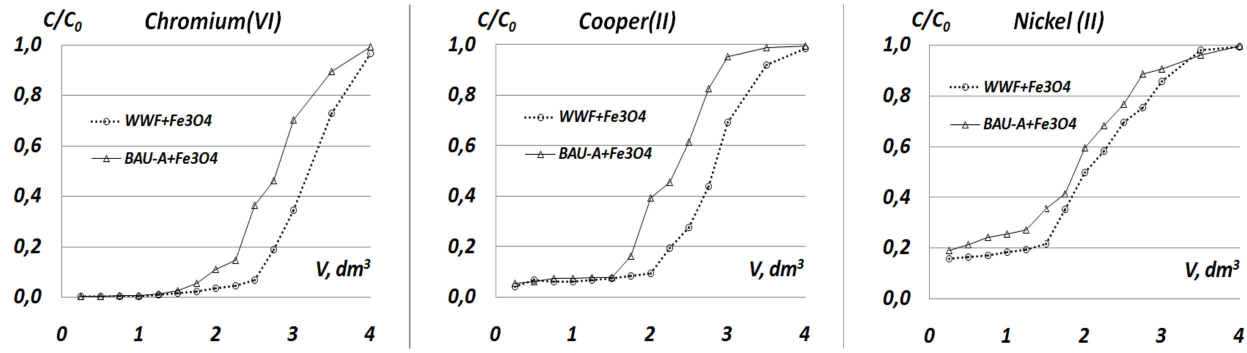

Fig.3. Graphs of sorption of heavy metal ions under dynamic conditions

According to the results obtained, the dynamic exchange capacity of WWF+Fe_3O_4 for Cr^{6+} is 5.92 mg/g, Cu^{2+} – 5.03 mg/g, Ni^{2+} – 3.61 mg/g, BAU-A+Fe_3O_4 for Cr^{6+} is 5.17 mg/g, Cu^{2+} – 4.10 mg/g, Ni^{2+} – 3.15 mg/g. The obtained values of the capacity of magnetic composite sorbents allow calculating the minimum dose of sorbent for post-treatment of galvanic wastewater (Table 4).

Table 4. Determination of the minimum dose of sorption material

Parameter	***Ion***		
	Cr^{6+}	Cu^{2+}	Ni^{2+}
C_0, mg/dm^3	4.23	0.79	1.16
C_2, mg/dm^3	0.03	0.50	0.10
MAC, mg/dm^3 [12]	0.05	1.00	0.25
D_{min} (WWF+Fe_3O_4), g/dm^3	0.62	0.05	0.19
D_{min} (BAU-A+Fe_3O_4), g/dm^3	0.67	0.05	0.22

Based on the obtained calculation results, the total minimum dose for post-treatment of galvanic wastewater from heavy metal ions for WWF+Fe_3O_4 is 0.86 g/dm^3, for BAU-A+Fe_3O_4 – 0.93 g/dm^3.

SUMMARY

The possibility of post-treatment of galvanic wastewater containing Cr^{6+}, Cu^{2+} and Ni^{2+} ions by the sorption method with the use of magnetic composite sorbents on the basis of waste wood fiber and activated carbon was studied. The factors, such as the temperature and the contact time of the phases, affecting the sorption properties of the samples were analyzed in static mode. The thermodynamic parameters of the sorption process were calculated, revealing a mixed mechanism of the adsorption process. It was established that the experimental data are correctly described by a pseudo-second-order model, implying that the chemical interaction stage is the limiting one. The experiments under dynamic conditions allowed us to reveal that the maximum dynamic exchange capacity for a modified wood fiber sample was 5.92 mg/g for Cr^{6+}, 5.03 mg/g for Cu^{2+}, and 3.61 mg/g for Ni^{2+}, which is superior to sorption of initial materials and is due to the presence of magnetite in the composition of modified samples.

CONCLUSION

Thus, the results presented in this paper show that the proposed method of modification of waste wood and activated carbon makes it possible to obtain composite materials possessing magnetic properties with sufficiently high sorption capacity that allows using the considered sorption materials for post-treatment of galvanic wastewater from heavy metal ions.

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REFERENCES

1. Kharlyamov D.A., Mavrin G.V., Sippel Y.A. About the possibility of sorption concentration of heavy metals using magnetite // Life Science Journal. –2014. – 11(8). – P. 607-610.

2. Malkin V.P. Technological aspects of treating industrial wastewater containing heavy metal ions. – Irkutsk: Publishing house of Irkutsk University. – 1991 – p. 63.

3. Fazullin D.D., Mavrin G.V., Shaikhiev I.G. Properties of cation-exchange membranes of nylon-PANI // Bulletin of the Technological University. – 2015. – V.18, No.12. – P. 194-197.

4. Alekseeva A.A., Fazullin D.D., Kharlyamov D.A., Mavrin G.V., Stepanova S.V., Shaikhiev I.G., Shaimardanova A.S. The use of leaves of different tree species as a sorption material for extraction of heavy metal ions from aqueous media (Review) // International Journal of Pharmacy and Technology. – 2016. – 8 (2). – P. 14375-14391.

5. Kharlyamov D.A., Mavrin G.V., Danilova E.A., Zinnatov R.R., Prytkova E.V., Dvoryak S.V. 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. – 2016. – 7 (3). – P. 1667-1670.

6. Denisova T.R., Shaikhiev I.G., Mavrin G.V., Sippel I.Y., Kuznetsova N.P. The influence of ash tree sawdust acid treatment on the removal of crude oil from water surfaces // Research Journal of Pharmaceutical, Biological and Chemical Sciences. – 2016. – 7 (5). – P. 1742-1750.

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

8. Kharlyamov D.A., Mavrin G.V., Shaikhiev I.G., Denisova T.R., Albutova D.A., Gafiyatova S.R. Preparation and application of a magnetic composite sorbent for collecting oil from a water surface // ARPN Journal of Engineering and Applied Sciences. – 2017. – Vol.12 No.5. – P. 1642-1648.

9. END F 14.1:2:4.135-98 Quantitative chemical analysis of waters. Method for performing measurements of the mass concentration of elements in samples of drinking, natural, sewage and atmospheric precipitation by atomic-emission spectrometry with inductively coupled plasma.

10. GOST 20255.2-89. Ionites. Methods for determining the dynamic exchange capacity.

11. Silaicheva M.V., Stepanova S.V., Shaikhiev I.G. Kinetics of iron (II) ions sorption by maple tree waste // Bulletin of Technological University. – 2015. – V.18. No.20 – P. 257-259.

12. Resolution of the Government of the Russian Federation of 03.11.2016 No. 1134 "On issues of implementation of cold water supply and water discharge".

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