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TÍTULO: Purificación por sorción de aguas residuales galvánicas de iones de hierro (Iii), cobre (Ii), cromo (Vi) y zinc (Ii) utilizando productos sólidos modificados de pirólisis de desechos que contienen carbono.

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RESUMEN: La capacidad de adsorción de los productos de pirólisis en azul de metileno se investiga en el espectrofotómetro UNICO 2800. El producto de pirólisis de sedimentos de lodo mostró propiedades de sorción a iones de metales pesados, con respecto a los iones de hierro, el grado de sorción fue de 99.8%, para el los iones de metales pesados investigados restantes oscilaron entre 35,4 y 77,6%. Para aumentar la actividad de sorción de los productos de pirólisis, se ha estudiado su activación por soluciones ácidas y alcalinas. Se determina que la solución alcalina aumenta la eficiencia de sorción de los productos de pirólisis en mayor medida.

PALABRAS CLAVES: pirólisis, desechos que contienen carbono, sorbente, carbón activado, aguas residuales, iones de metales pesados.

TITLE: Sorption purification of galvanic wastewater from Iron (Iii), Copper (Ii), Chromium (Vi) And Zinc (Ii) Ions Using Modified Solid Products of Pyrolysis Of Carbon-Containing Waste.

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ABSTRACT: The adsorptive ability of products of pyrolysis on methylene blue is investigated on the spectrophotometer UNICO 2800. The product of pyrolysis of sludge sediments showed sorption properties to ions of heavy metals, with respect to iron ions, the degree of sorption was 99.8%, for the remaining investigated heavy metal ions it ranged from 35.4 to 77.6%. To increase the sorption activity of pyrolysis products, their activation by acid and alkali solutions has been studied. It is determined that the alkali solution increases the sorption efficiency of pyrolysis products to a greater extent.

KEY WORDS: pyrolysis, carbon-containing wastes, sorbent, activated carbon, wastewater, heavy metal ions.

INTRODUCTION.

The spread of pollutants in the environment has become global. The problem of preventing harmful effects and purification from pollutants is currently relevant for the whole world.

Heavy metal ions are classified as priority substances that pollute the biosphere and have toxicity at low concentrations. In addition to direct toxic effects on living and plant organisms, heavy metal ions tend to accumulate, which increases their danger to biological organisms. When entering water bodies, they are in the most dangerous ionic form for a long time and, even passing into a bound state (colloid form, bottom sediments or other poorly soluble compounds) continue to pose a potential threat to hydrobionts.

The main anthropogenic source of heavy metal ions entering the environment is galvanic production.

The main way to reduce the negative impact of galvanic production on the environment is to treat wastewater from heavy metal ions before discharging them into water bodies. The methods of wastewater treatment, which have found application in the treatment plants of galvanic plants, are usually divided into: mechanical, physico-chemical, chemical and electrochemical, etc. In a market economy, it is more profitable for enterprises to follow the path of greening the water economy. The decrease in the amount of sewage can be facilitated by the use of new production technology, which will require considerable material costs, which are unrealistic for many enterprises financially. As a result, there is another way - the introduction of highly efficient and low-cost methods of cleaning contaminated water resources (Yusupova, 2015).

In connection with the foregoing, research and development of simple and technological ways of cleaning polluted water from industrial enterprises from heavy metal ions are of undoubted interest.

DEVELOPMENT.

Methods.

The mass was measured on laboratory scale Ohays RV 512 and analytical scale RV 214. The ionomer ANION 4100 was used to measure the pH of the solutions. The mineralization and specific electrical conductivity were measured with an conductometer ANION-7020 (Ilnar, Nasyrov, Vilnus, Ahmetov, Munir, Miftahov, Gennady, Mavrin, Sokolov, 2016).

Assessment of adsorption was carried out based on the results obtained by the method of determining the adsorption of methylene blue (Fazullin, Mavrin, Melkolvan, 2014). Adsorption of methylene blue gives an idea of the surface of the sorbent formed by pores with a diameter greater than 1.5 nm.

An indicator solution with a mass concentration of 1500 mg / dm3 was prepared for the analysis. A sample of semi-coke weighing 0.1 g was placed in a conical flask, 25 ml of a methylene blue solution was poured in, capped and shaken for 20 minutes. After centrifugation for 15 min. 1 cm3 was pipetted, transferred to a volumetric flask with a capacity of 100 cm 3 and diluted with distilled water to a label.

Adsorption activity of coal in indicator X was calculated by the formula:

$$X = \frac{(C_1 - C_2 \cdot K) \cdot 0{,}025}{\mathrm{m}} \quad , (1)$$

где:

C_1 – mass concentration of the initial solution of the indicator, mg / dm3;

C_2 – mass concentration of the solution after contact with semi-coke, mg / dm3;

К – the dilution factor of the solution taken for analysis after contacting the carbonaceous material, К = 100;

m – weight of a sample of coal, г;

0,025 – volume of methylene blue solution taken for clarification, дм^3.

Studies of the adsorption capacity of pyrolysis products on methylene blue were carried out on a UNICO 2800 spectrophotometer in the spectral range of 400 nm. The error in determining the transmittance is 0.5%.

Sorption properties of pyrolysis products with respect to heavy metal ions were studied by atomic-emission spectrometry with inductively coupled plasma on an spectrometer Agilent 720-OES

(Sorption properties of carbon waste pyrolysis product for biological wastewater treatment. 2016).

Activation of pyrolysis products of carbon-containing waste was carried out by chemical reactivation. As activating agents were used solutions of hydrochloric, sulfuric acids and sodium hydroxide. The concentration of solutions ranged from 1 to 15%.

For activation in the conical flasks was placed a sample of semi-coke with a mass of 10 g and 200 ml of the corresponding solution of acids and alkali. Next, stirring was carried out on the shakers for 30 minutes. Semi-coke was extracted from the solution and washed with distilled water. The resulting sample was dried for 24 hours at room temperature (Cation-exchange membranes with polyaniline surface layer for water treatment / D2014).

Solutions for activation were studied for the content of heavy metal ions.

Results and discussion.

As objects of research in this article are taken samples of products of pyrolysis processing of carbon-containing wastes, obtained at the installation of low-temperature pyrolysis of the complex for processing sludge deposits by the method of continuous pyrolysis.

Pyrolysis was subjected to the following carbon-containing wastes: sludge, wood waste, rubber waste (worn automobile tires). The resulting solid pyrolysis product was studied as a potential sorbent for wastewater treatment from heavy metal ions.

The toxicity of pyrolysis products by biotesting. Products pyrolysis of sludge, wood waste and rubber waste belong to the IV (fourth) class of hazard (Ilnar, Nasyrov, Gennady, Mavrin, Aliya, Ahmetshina, Aigul, Ahmadieva, 2017).

Sorption properties of pyrolysis products of carbon-containing wastes with respect to iron, copper, manganese and chromium ions under static conditions are studied. The best sorption ability with respect to iron, manganese, copper and chromium ions compared to BAU coal was the product of pyrolysis of sludge sediments (99.8%, 35.4%, 77.6%, 74.6%, respectively) (Ilnar, Nasyrov, Gennady, Mavrin, Aliya, Ahmetshina, Aigul, Ahmadieva, 2017).

The adsorption was evaluated on the basis of the results obtained with the methylene blue adsorption determination technique.

The results are shown in table 1.

Table 1. Adsorption activity by methylene blue

samples	X, mg / g
solid product of pyrolysis of sludge	133.2
solid product of pyrolysis of wood waste	32.8
solid product of pyrolysis of rubber waste	33.6
BAU	213.7
standard	225

Adsorption activity for methylene blue for pyrolysis products is in all cases less than the normative value. This means that non-activated pyrolysis products can be a satisfactory sorbent only to a certain list of sorbates, which must be investigated in each specific case.

The analysis of literary data shows that for process of activation of carboniferous raw materials acids, the strong bases or salts generally use, apply alkaline activation in the presence of sodium hydroxide (GOST 4453-74 Coal the active clarifying wood powdery. Specifications; Materials, 2008; Saravanane. Sundararajan. Reddy, 2002).

During the washing of the pyrolysis products from the activating solutions, the parameters of distilled water used for washing were monitored. The results of the analysis of the final wash from activating solutions indicate that there is no residual amount of activator.

Preliminary solutions for activation were investigated for the content of heavy metal ions. The results are shown in table 2.

Table 2. The content of heavy metal ions in activating solutions.

heavy metal ions	concentration, mg / l		
	sulfuric acid	hydrochloric acid	sodium hydroxide
Mn	0.463	0.047	0.001
Fe	0.046	0.740	0.001
Zn	0.107	0.399	0.003
Cu	0.002	0.006	0.001
Cr	0.010	0.010	0.001
Ni	0.002	0.002	0.001

The results of the studies indicate the insignificant presence of heavy metal ions in solutions for activation, which allows us to conclude that there is no contamination of sorption materials by the activator.

Table 3 presents the results of measurements of the mass fraction of ash from pyrolysis products before and after activation. The obtained data indicate that after the activation of the pyrolysis products the ash content on average decreased by 30% for the sludge, by 40-45% for rubber waste and wood waste.

Table 3. Mass fraction of ashes of sorbents.

samples	ash content, %
solid product of pyrolysis of sludge not activated	46.9
solid product of pyrolysis of sludge activated 1% HCl	30.4
solid product of pyrolysis of sludge activated 1% H_2SO_4	30.8
solid product of pyrolysis of sludge activated 1% NaOH	33.2
solid product of pyrolysis of wood waste not activated	40.3
solid product of pyrolysis of wood waste activated 1% HCl	22.4
solid product of pyrolysis of wood waste activated 1% H_2SO_4	26.6
solid product of pyrolysis of wood waste activated 1% NaOH	22.1
solid product of pyrolysis of rubber waste not activated	50.2
solid product of pyrolysis of rubber waste activated 1% HCl	26.3
solid product of pyrolysis of rubber waste activated 1% H_2SO_4	30.5
solid product of pyrolysis of rubber waste activated 1% NaOH	23.3

Table 4 shows the results of pH, mineralization and specific electrical conductivity (SEC) measurements of the aqueous extract of the sorbents.

Table 4 - Indices of water extract of sorbents.

activator	mineralization, mg / l	SEC, μS / cm	pH, unit pH
solid product of pyrolysis of sludge			
HCL 1%	96.8	201.1	3.50
$H_2SO_4$1%	208.7	433	3.35
NaOH 1%	50.4	107	8.74
solid product of pyrolysis of wood waste			
HCL 1%	89.2	187.6	5.67
$H_2SO_4$1%	190.7	397	4.60
NaOH 1%	48	102.9	8.19
solid product of pyrolysis of rubber waste			
HCL 1%	36.5	77.8	6.51
$H_2SO_4$1%	30.9	66.3	6.67
NaOH 1%	23.2	49.5	7.35

The data obtained during the determination of the indices of aqueous extract indicate that activation of the pyrolysis products with acid markedly increases the mineralization and reduces the pH. Probably, acids dissolve some components of the solid phase of pyrolysis products.

With the activation of alkali, the mineralization practically did not change, the pH increased. It is known that in an alkaline medium the solubility of heavy metal ions decreases with the formation of insoluble compounds of metal ion.

To determine the adsorption of activated pyrolysis products of carbon-containing wastes, the technique presented in GOST 4453-74 was chosen. This standard implies the determination of the adsorption activity of powdered activated carbon, the value of which should correspond to the norm and be at least 225 mg/g.

The results are shown in table 5.

In the course of the data obtained, it can be concluded that the solid pyrolysis product activated with an alkaline solution of sodium hydroxide showed the best adsorption activity for methylene blue and exceeds the BAU by 23% for the product of pyrolysis of mud sediments and 18.9% for wood waste.

When comparing the clarifying power of pyrolysis products with methylene blue before activation, the results obtained increased with activation of H_2SO_4-1% by 4 times, with HCl-1% by 5 times, with HCl-3% by 4.5 times, with NaOH-1% 7.7 times for pyrolysis products of wood waste.

Thus, the adsorption activity of the obtained sorption materials makes them promising for water purification from pollutants.

Table 5. Adsorption activity by methylene blue after activation.

samples	X, mg/g
solid product of pyrolysis of sludge – 1 % H_2SO_4	149.2
solid product of pyrolysis of sludge – 1 % HCl	173.4
solid product of pyrolysis of sludge – 3 % HCl	92.7
solid product of pyrolysis of sludge – 1 % NaOH	262.1
solid product of pyrolysis of wood waste – 1 % H_2SO_4	133.1
solid product of pyrolysis of wood waste – 1 % HCl	165,3
solid product of pyrolysis of wood waste – 3 % HCl	149.2
solid product of pyrolysis of wood waste – 1 % NaOH	254
solid product of pyrolysis of rubber waste – 1 % H_2SO_4	141.1
solid product of pyrolysis of rubber waste – 1 % HCl	181.5
solid product of pyrolysis of rubber waste – 3 % HCl	84.7
solid product of pyrolysis of rubber waste – 1 % NaOH	189.5
Норматив (7)	225.0

Sorption activity of sorbents with respect to ions of heavy metals: Fe, Cu, Cr, Zn was studied in model solutions in the static regime, which were prepared by dissolving the salts of the corresponding metals in distilled water. The results of determining the initial and final concentrations of heavy metal ions by atomic emission spectroscopy are presented in tables 6 and 7.

Table 6. Mass content of heavy metal ions after activation.

samples	concentration, mg / l			
	Fe	Cu	Cr	Zn
initial solution	38.9	39.3	31.6	27.7
filtrate after a solid product of pyrolysis of sludge – 1% HCl	12.8	23	24	19
filtrate after a solid product of pyrolysis of sludge – 3% HCl	15.2	15.9	13.9	17.8
filtrate after a solid product of pyrolysis of sludge – 1% NaOH	0.140	1.77	0.350	0.480
filtrate after a solid product of pyrolysis of wood waste – 1% HCl	17	20.6	26.5	19.4
filtrate after a solid product of pyrolysis of wood waste – 3% HCl	19.7	28.9	25.8	11.1
filtrate after a solid product of pyrolysis of wood waste – 1% NaOH	0.010	13	9.92	9.93
filtrate after a solid product of pyrolysis of rubber waste – 1% HCl	9.63	25.2	24	19.9
filtrate after a solid product of pyrolysis of rubber waste – 3% HCl	22.1	28.1	28.1	23.9
filtrate after a solid product of pyrolysis of rubber waste – 1% NaOH	8.55	18.9	20.5	17
filtrate after BAU	0.020	0.010	4.91	0.020

Table 7. Degree of sorption after activation.

samples	degree of sorption, %			
	Fe	Cu	Cr	Zn
solid product of pyrolysis of sludge – 1% HCl	67	41.4	23.8	31.3
solid product of pyrolysis of sludge – 3% HCl	60.8	59.6	55.6	35.5
solid product of pyrolysis of sludge – 1% NaOH	99.8	95.5	98.8	98.3
solid product of pyrolysis of wood waste – 1% HCl	56.2	47.6	16.2	30.1
solid product of pyrolysis of wood waste – 3% HCl	49.4	26.5	18.1	59.9
solid product of pyrolysis of wood waste – 1% NaOH	99.9	66.9	68.6	64.1
solid product of pyrolysis of rubber waste – 1% HCl	75.2	35.9	23.9	28.3
solid product of pyrolysis of rubber waste – 3% HCl	43.3	28.5	11	13.5
solid product of pyrolysis of rubber waste – 1% NaOH	78	51.6	35.1	38.4
BAU	99.9	99.9	84.5	99.9

The best sorption ability with respect to heavy metal ions in comparison with BAU coal was shown by the sorbent obtained from the pyrolysis product of the sludge, activated with sodium hydroxide. After studying the sorption properties of the activated pyrolysis products, sorbents with the best results after activation were chosen.

Subsequently, sorption isotherms were constructed using the standard method for determining the sorption capacity of the sorbent under optimal conditions for ions of heavy metals (Fe^{3+}, Cu^{2+}) . The results are shown in tables 8 and 9.

Table 8. Sorption iron ions (pyrolysis product is activated sludge by solution of sodium hydroxide).

initial concentration, mg / l	concentration after sorption, mg / l	degree of sorption, %
0.032 ± 0.005	0.002	95.2
0.624 ± 0.094	0.042	93.3
6.81±1.02	0.950	86.0
83.9 ± 12.6	19.1	77.3
145 ± 22	65	54.9
331 ± 50	217	34.4
767 ± 115	621	18.9
1367 ± 205	1206	11.8
1881 ± 282	1710	9.10
3900 ± 585	3730	4.40

Based on the values obtained (Table 8), the sorption capacity (a, mg / g) was calculated. The results are shown in Table 9.

Table 9. Sorption capacity

initial concentration, mg / l	a, mg/g
0.032	0.002
0.624	0.029
6.81	0.293
83.9	3.24
145	3.98
331	5.69
767	7.26
1367	8.05
1881	8.57
3900	8.49

And the graph was plotted in coordinates: "sorption capacity - the initial concentration" (Fig. 1).

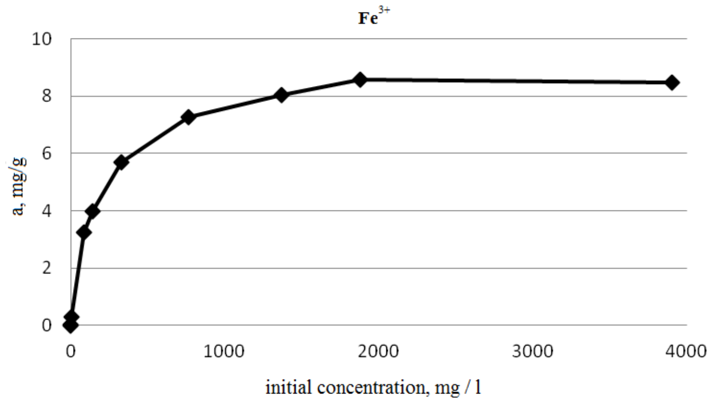

Figure 1. Isotherm of sorption of iron (III) ions.

The data on the analysis of the isotherm (Fig. 1) suggests that at the saturation point their projections on the ordinate axis indicate the value of the sorption capacity relative to the iron ions. It is determined that the maximum sorption capacity is 8.37 mg/g.

Table 10. Sorption of copper ions (pyrolysis product is activated sludge by solution of sodium hydroxide).

initial concentration, mg / l	concentration after sorption, mg / l	degree of sorption, %
0.064 ± 0.010	0.001	97.9
0.591 ± 0,089	0,027	95.5
5.39 ± 0.81	0.330	93,9
66.8 ± 10.0	7.1	89.4
138 ± 21	54	60,9
286 ± 43	151	47.3
637 ± 96	439	31.1
955 ± 143	743	22.1
1348 ± 202	1127	16.4
2430 ± 365	2210	9.10

Table 11. Sorption capacity

initial concentration, mg / l	a, mg / g
0,064	0,003
0,591	0,028
5,39	0,253
66,8	2,98
138	4,21
286	6,75
637	9,90
955	10,6
1348	11,0
2430	11,0

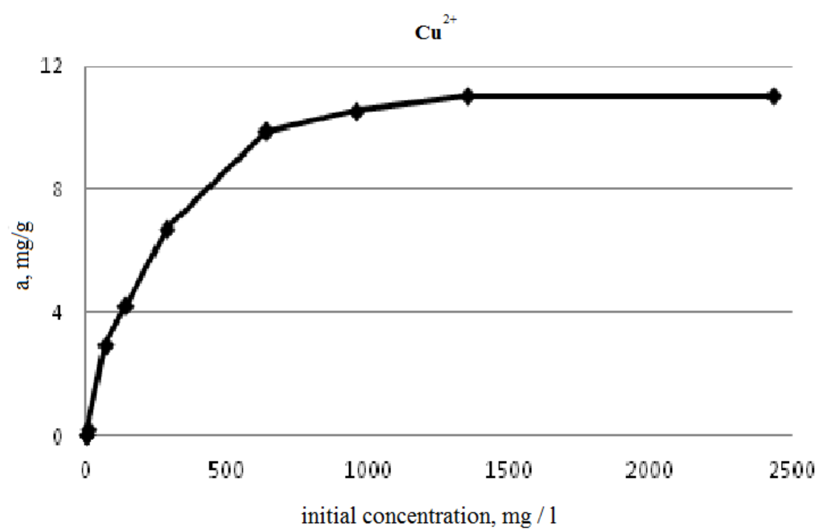

Figure 2. Isotherm of sorption of copper (II) ions

The sorption capacity for copper is 10.9 mg / g.

Table 12 gives the sorption characteristics of carbon adsorbents for comparison (Removal of the heavy metal ion Cr(VI) by soybean hulls in dyehouse wastewater treatment (Sheng-quan Ye, Guo Si-yuan, Yu Yigang, 2012).

Table 12. Sorption characteristics of carbon adsorbents

adsorbent	a, mg / g	
	Fe^{3+}	Cu^{2+}
BAU-A	-	3.30
AYV	-	12.2
OAYV-sulfuric	13.5	12.7
OAYV-nitric	10.2	16.6

CONCLUSIONS.

1. Samples of solid products of pyrolysis of sludge, wood waste and rubber waste were obtained by means of low-temperature pyrolysis under production conditions.

2. The method of biotesting showed that the obtained pyrolysis products belong to the IV (fourth) class of hazard.

3. The product of pyrolysis of sludge sediments showed sorption properties to ions of heavy metals, with respect to iron ions, the degree of sorption was 99.8%, for the remaining investigated heavy metal ions it ranged from 35.4 to 77.6%.

4. To increase the sorption activity of pyrolysis products, their activation by acid and alkali solutions has been studied. It is determined that the alkali solution increases the sorption efficiency of pyrolysis products to a greater extent.

5. It is established that the activated product of pyrolysis of sludge on the level of efficiency doesn't concede to a commodity sorbent of heavy metals of the BAU brand.

6. Heavy metal sorption isotherms were obtained, the maximum specific adsorption for Fe^{3+} ions was 8.37 mg/g, Cu^{2+} - 10.9 mg/g for pyrolysis products of sludge activated by sodium hydroxide.

Thus, alkali-activated products of sludge pyrolysis are promising sorbents for the recovery of heavy metals from wastewater and in sorption capacity are slightly inferior to carbon adsorbents.

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