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STUDIES ON THE EFFICIENCY OF WATER PURIFICATION FROM HEAVY METAL IONS USING MAGNETITE OBTAINED FROM TECHNOGENIC WASTE

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Abstract*: The study dwells on the effectiveness of application of magnetite from technogenic waste for treatment of wastewater from heavy metal ions. In order to assess the significance of the influence of the main factors affecting the efficiency of waste treatment we made the analysis of variance.*

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Introduction

At present, there is no single method for treating wastewater for all types of pollution. Wastewater treatment is conducted by a combination of different methods, as new substances, new technological processes. Also new compositions are developed. The choice of method depends on the composition of the wastewater, the concentration of pollutants, the requirement and possibility of reuse of the treated water, and the inflow regime.

Galvanic production is the one of the most environmentally damaging one. The main danger occurs in various bodies of water. Such production releases a lot of wastewaters, which poses the maximum level of threat. This water contains many impurities with heavy metals, alkaline composition and other highly toxic compounds [1].

Mechanical engineering widely uses electroplating technology [2]. Chemical coatings and pre-treatment operations, chemical wastage with washings is sometimes tens of times greater than surface treatment [3]. Washing water consumption after preparatory operations is 3-7 times higher than the same for plating [4].

The main substances to be neutralized are hexavalent chromium compounds, cyanides (CN^-), ions of heavy and non-ferrous metals: Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Sn^{2+}, Pb^{2+}.

Nowadays there are several known methods of treating water from various contaminants using magnetite as a sorbent or as an integrated element into various sorbents [5]. Magnetite is used as an active layer in streamline filters [6] or as a sorbent with further removal of bound particles by magnetic separation means [7].

Today the innovation of methods for the treatment of galvanic wastewater is very important. And the treatment of water from heavy metal ions after galvanic workshops with magnetite is a very relevant issue for most of the companies. The main advantage of the magnetite is its utility, the simplicity of obtaining from technogenic waste, environmentally sustainability and high purity.

The study dwells on the effectiveness of application of magnetite from technogenic waste for treatment of wastewater from heavy metal ions.

Magnetite was produced by the thermal carbon treatment of iron-containing waste (ICW). Waste activated carbon from the Federal Waste Catalogue: code 4.42.104.01.49.5 "Activated coal, used in drying air and gases and not contaminated with hazardous substances" was used as a reducing agent. The exhausted activated carbon was crushed, sieved through a 63 μm sieve and injected into the ICW paste at a dry matter ratio of 1:2. Sodium carbonate was added to create an inert environment for its decomposition at recovery temperatures. Heat treatment of the mixture was conducted in a trizonal cylindrical roaster: 1st zone - heating to 900 °C, 2-nd zone - holding at 900 °C for one hour, 3-rd zone - cooling to 50 °C.

For statistical analysis of the results, we use methods of variance and regression analysis [8].

Main body

The objects of research were industrial (technogenic) wastes (dust from electrostatic precipitators of "Severstal" Cherepovets metallurgical plant, galvanic sludge, sludge from deironing of groundwater), magnetite from wastes, and wastewater from electroplating plant.

Table 1 shows the main characteristics of plating pollutants of a given composition [9]. The physico-chemical properties of iron-containing waste are given in Table 2 [10].

Table 1. Characteristics of pollutants

Substance	MPC (mg/dm^3)	Class of hazard	Sources	Health effect
Copper (Cu) Cu^{2+}	0.5	3	Galvanizing plant, coppering	Mutagenic or toxic effect It has an irritant effect on the mucous coats of the upper air passages.
Cadmium (Cd) Cd^{2+}	0.001	2	Galvanizing plant, cadmium coating, galvanized pipes corrosion	Increasing of cardiovascular diseases (CVD), nephritic and cancer incidence, problems with ovarian menstrual cycle (OMC), wrong gestation course, mortinatality, osseous lesion.
Nickel (Ni) Ni^{2+}	0.5	3	Galvanizing plant, nickeling	Disorders of central and autonomic nervous system, pulmonary and cerebral edema, tachycardia, anemia, carcinoma of lung.

Table 2. The physico-chemical properties of iron-containing waste

Name of Parametre	Waste of "Severstal", Cherepovets, Vologda region, Russia	Galvanic sludge, "Vympel", Rybinsk, Yaroslavl region, Russia	Galvanic sludge, Yaroslavl Shipbuilding Plant, Yaroslavl region, Russia	Waste of "Olenegorsk Mining and Processing Plant", Olenegorsk, Murmansk region, Russia	Waste of "Severstal", Cherepovets, Vologda region, Russia (after etching)	Deposit after the deferrization of groundwater
FeO	2,1±0,50	-	-	26,7±0,70	47,8±5,60	-
Fe_2O_3	76,96±0,77	51,7±2,60	55,7±2,80	63,4±1,90	1,6±1,00	60.20
CaO	2,15±1,34	2,9±0,40	8,1±1,20	0,60±0,008	0,09±0,05	14.30
Na_2O	0,14±0,07	-	-	0,063±0,001	-	-
ZnO	3,17±0,76	3,87±1,00	2,60±0,70	-	-	12.20
$C_{general}$	0,44±0,05	-	-	-	-	-
CuO	0,22±0,01	0,33±0,09	0,10±0,06	-	-	0.58
P_2O_5	0,15±0,01	-	-	0,025±0,001	-	-
SiO_2	1,59±0,35	-	-	7,75±1,10	-	4.10
$Cr_{general}$	-	1,84±0,87	2,9±1,20	-	-	-
NiO	traces	0,15±0,10	0,41±0,30	-	-	0.25
$H_2SO_{4\ free}$	-	-	-	-	2,9±0,02	-
MgO	-	-	-	-	-	7.80
Loss by roasting 600 ^{0}C, %	2,1±0,50	24,8±1,90	21,0±2,10	0,53±0,10	45,8±0,30	
Mass content of substances non-dissolved in HCl, %	10,10±4,60	6,8±0,20	5,53±0,30	-	1,81±0,010	
Mass content of substances dissolved in H_2O, %	1,2±0,30	7,6±0,50	3,7±0,90	0,9±0,50	-	

The study of the magnetic properties of the resulting magnetic phase and magnetic fluids was conducted by a vibrating magnetometer [11]. The scheme is shown in Fig. 1.

Sample 1, which is a cuvette with magnetic fluid [12] or its dispersed phase, was attached to the end of a rod of non-magnetic material 2. The other end of the rod was rigidly fixed to the diffuser of electromagnetic vibrator 3. The vibrator was powered by a GZ-112 low-frequency signal generator. The sample was placed between the poles of electromagnet 4.

Four identical measuring coils were placed between the pole terminals of the

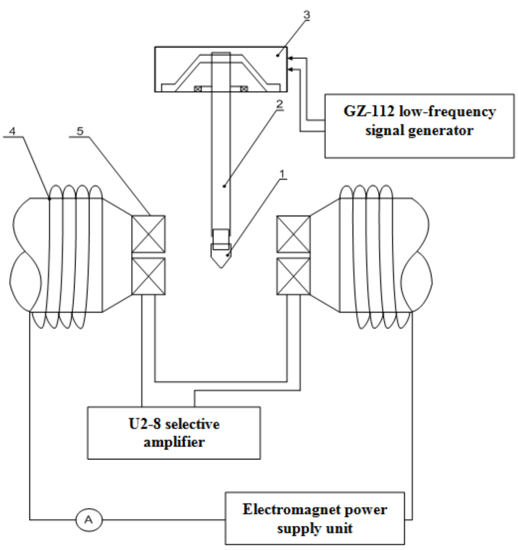

Fig.1. Scheme of the vibration magnetometer: 1 - sample cuvette; 2 - rod of non-magnetic material; 3 - vibrator; 4 - electromagnet; 5 - measuring coils

electromagnet and switched in pairs towards each other 5 in which an EMF of induction proportional to the saturation magnetization of the sample was induced when the sample oscillated (with a frequency of 81 Hz). This signal was input to the U2-8 selective amplifier and was recorded.

The unit was calibrated with a reference sample (electrolytic nickel, 56 mg). The sensitivity of the system was $4 \cdot 10^{-3} \cdot m^2/kg$ and the measurement error did not exceed 3%.

The efficacy of wastewater treatment was conducted by determining the concentration of heavy metals in the samples before and after treatment using standard methods [13-17]. The concentration of heavy metal ions was assessed on the basis of the graduation dependence of the concentration of standard solutions *C* on their optical density *D*, measured using a KFK-2 photocolorimeter. These dependencies were approximated by a linear regression equation

$$C = kD, \tag{1}$$

where *k* is a linear regression coefficient calculated by the method of least squares on the basis of samples obtained from standard solutions.

The concentration of the test solution was determined by substituting its optical density into equation (1).

The significance of the influence of the main factors affecting the efficiency of waste treatment was assessed by means of analysis of variance.

Table 3 shows the results of the analysis of variance to assess the significance of the effect on the cleaning efficiency of the ratio of magnetite to chromium (VI) ions.

Table 3. Test of the relevance of the effect of the ratio of magnetite to chromium (VI) ions on efficiency of purification, %

Parallel measurements	Cr (VI)/magnetite ratio					
	1/2	1/4	1/6	1/8	0.1	0
Test 1	4.546	28.563	66.334	85	86.997	88.032
Test 2	5.01	26.775	68.245	86 2/3	88.035	89.01
Test 3	4.889	29.64	66	85 3/7	87.495	87.5
Test 4	5.026	30.005	67.211	86.422	87.3	88.1
Average	4.868	28.746	66.948	85.874	87.457	88.161
Dispersions	0.050	2.101	1.009	0.626	0.191	0.393
Error factor variance	0.728					
Factor variance	7536.356					
Dispersion ratio *F*	10350.579					
Critical value	2.621					
Conclusion on the relevance	Relevant					

This arrangement of the responses (degree of purification) in the table, the dispersion between columns is due to the influence of a factor (Cr (VI)/magnetite ratio), the dispersion within columns is due to the influence of random factors.

The effect of the randomness factor is evident in the dispersion of responses at each level of the factor relative to the average $\grave{y}_i$:

$$\grave{y}_i = \frac{1}{n}\sum_{j=1}^{n} y_{ji}. \tag{2}$$

The randomness factor can be assessed by calculating the variance of reproducibility at each level of the factor:

$$s_{\varepsilon l}^2 = \frac{1}{n-1}\sum_{j=1}^{n}(y_{ji} - \grave{y}_i)^2. \quad (3)$$

Generally, when performing analysis of variance, it is assumed that the accuracy of the response measurement does not vary between experiments. The variances $s_{\varepsilon l}^2$ should therefore be assessed by the same general variance σ_{ε}^2. This can be verified by comparing the significance of the difference between the maximum and minimum of the variance $s_{\varepsilon l}^2$ by Fisher's test. The difference will be insignificant if the inequality is met:

$$\frac{s_{\varepsilon \max}^2}{s_{\varepsilon \min}^2} \leq F(n-1, n-1, q), \quad (4)$$

where $F(n-1, n-1, q)$ is quantile of the Fisher distribution for the number of degrees of freedom of the variances compared $l_1 = n - 1$, $l_2 = n - 1$ and the selected relevance level q.

If the inequality is met, all other variances also differ insignificantly and can be averaged, thus calculating the variance of the error:

$$s_{\varepsilon}^2 = \frac{1}{k}\sum_{l=1}^{k} s_{\varepsilon l}^2. \quad (5)$$

The influence of a factor can be assessed using variance:

$$s^2 = \frac{n}{k-1}\sum_{l=1}^{k}(\grave{y}_l - \grave{y})^2, \quad (6)$$

where ỳ – the average of all observations.

To check the relevance of the effect of a factor on the variance s^2 must be compared by Fisher's test with the variance of the error s_{ε}^2:

$$\frac{s^2}{s_{\varepsilon}^2} \leq F(n-1, n-1, q). \quad (7)$$

If inequality (7) is not fulfilled, then the null hypothesis of the variance difference is rejected s^2 and s_{ε}^2 the influence of the factor should be considered as the relevant one [8].

By Table 3, the highest degree of purification is observed when the ratio of magnetite to chromium (VI) ions is 1/8, 1/10 and 1/15.

Similarly, a variance analysis was conducted on the dependence of wastewater treatment efficiency on magnetite calcination time. Results are shown in Table 4.

Table 4. Test of the relevance of the effect of magnetite calcination time at T = 900 °C on purification efficiency, %

Parallel measurements	Calcination time, hours			
	1	2	3	4
Test 1	86.974	80.997	2.16	1.05
Test 2	87.353	81.267	1.97	0.873
Test 3	88.02	83.4	1.993	1.134
Test 4	87.22	81.315	2.018	1.15
Average	87.392	81.745	2.035	1.052
Dispersions	0.200	1.237	0.007	0.016
Error factor variance	0.365			
Factor variance	9212.716			
Dispersion ratio F	25226.490			
Critical value	3.239			
Conclusion on the relevance	Relevant			

Table 4 shows that when magnetite calcinated for more than 2 hours is used, the efficacy of the wastewater treatment decreased rapidly. The use of magnetite calcinated for 1 h at 900 °C is more efficient and economical.

The dependence of water purification efficiency on mixing and shaking time with the adsorbent (magnetite) was further investigated.

As the analysis shows, an effective purification rate of 89% is achieved with an agitator and a mixing time of 15 minutes. When shaking, the water purification efficiency is 85%.

The effect of magnetite activation on the efficacy of wastewater treatment was investigated. The activation was conducted in a variable magnetic field.

Activated and inactivated magnetite, obtained from iron-containing waste, were used as adsorbents in the treatment of chrome-containing wastewater. Results are shown in Table 5.

Table 5. Checking the relevance of the effect of magnetite activation on the treatment efficiency of chrome-containing wastewater, %

Parallel measurements	No activation	Activated "Contour" 1, min	Activated "Microwave oven" 2, min
Test 1	88.549	97.11	93.041
Test 2	89.117	96.142	90, 959
Test 3	89.02	98.061	92.431
Test 4	89.23	96.037	92, 415
Average	88.979	96.838	92.736
Dispersions	0.090	0.899	0.186
Error factor variance		0.391	
Factor variance *A*		46.347	
Dispersion ratio *F*		118.416	
Critical value		4.459	
Conclusion on the relevance		Relevant	

By Table 5, the highest efficiency is achieved using magnetite sorbent activated on "Contour" unit (voltage - 75 V, frequency - 50 Hz, magnetic induction - 0.11 Tesla, time - 2 min) is 96%.

It is important to note that a purification efficiency of over 90% is achieved on magnetite particles having the iron (II) hydroxide shell. In a ferromagnetic suspension, the resulting chromium (III) hydroxide is stayed on the magnetite. The shell consists of hydroxyl ions and iron (II) hydroxides, contributing the deoxidization of Cr^{6+} to Cr^{3+}. The adhesion forces are the main interaction forces in the treatment of wastewater from heavy metal ions using magnetite as a precipitant due to ionic-electrostatic, magnetic and molecular interactions.

The obtained magnetite was also used for the treatment of nickel-containing, copper-containing and zinc-containing wastewater. The efficiencies of the wastewater treatment are shown in Table 6.

Table 6. Test of the relevance of the influence of heavy metal ions on the efficiency of wastewater treatment (WWT) with magnetite (in %)

Parallel measurements	Wastewater with heavy metal ions		
	Wastewater with Ni ions	Wastewater with Zn ions	Wastewater with Cu ions
Test 1	40.749	92.36	89.524
Test 2	44, 994	95, 84	90.675
Test 3	46.095	96, 092	92.846
Test 4	48.15	96.753	93.22
Average	44.998	94.557	91.566
Dispersions	14.596	9.649	3.113
Error factor variance		9.119	
Factor variance *A*		2316.794	
Dispersion ratio *F*		254.052	
Critical value		4.459	
Conclusion on the relevance		Relevant	

Probably, the influence of interfering ions in the analysis of the treated water (water analysis was conducted both by photometric with dimethylglyoxime and titrimetric methods) provides the low treatment efficiency of nickel-containing wastewater [18].

Conclusions

1. One of the actual problems of industrial enterprises, having in their technological cycle galvanic processes, remains the problem of deep wastewater treatment from heavy metal ions. The wastewater from the plating industry is considered to be multi-element. Chromium, zinc, copper and nickel are considered to be the main substances of concern to the environment. Nowadays, a great attention is paid to sorption methods for the treatment of industrial wastewater. One of the current trends is the production of relatively inexpensive sorption materials. The use of magnetite obtained from technogenic waste can be effective for the treatment of wastewater from heavy metal ions.

2. We assessed the physico-chemical properties of technogenic iron-containing wastes used as secondary material resources for magnetite production. By the tests, the waste contains more than 50% iron ions in terms of Fe_2O_3.

3. We study the possibility of using the produced magnetite as an adsorbent for water purification from heavy metal ions. The main advantages of magnetite are its low cost and large available amounts. Moreover, magnetite is characterized by its ability to precipitate in a magnetic field, making it easier to separate from purified water.

4. We experimentally show the high efficiency of wastewater treatment containing heavy metal ions. For chrome-containing, zinc-containing, copper-containing wastewater the treatment efficiency is 90-96%.

5. Magnetite activation in an electromagnetic field increases water purification efficiency by 5-7%.

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