Copper and Nickel Substances Extraction from Water Mediums by Waste of Disaccharide Production

Natalia Sergeevna Lupandina, Zhanna Anuarovna Sapronova,
SvetlanaVasilievna Sverguzova and Valeriy Stanislavovich Lesovik
Belgorod State Technological University Named after V.G. Shoukhov,
Kostyukov Str. 46, 308012 Belgorod, Russian Federation

Abstract: The study describes an integrated approach to solving the problem of disposing of various industrial wastes in which for wastewater treatment is proposed to use solid waste sugar industry defecate. This issue is actual because every year only on the territory of CIS countries millions of cubic meters of untreated sewage dumped in water bodies and accumulated solid industrial waste which are insufficiently involved in the refining process. The approach proposed by researchers is the most rational from the point of view of environmental protection and natural resource use because this wastewater treatment used physicochemical properties of the substances included in the solid waste and waste themselves are used as raw materials. On the example of laboratory research and testing in an industrial condition researchers convincingly demonstrated perspective of the proposed method of treatment. The study may be interesting to specialists in the field of wastewater treatment and recycling.

Key words: Wastewater treatment, heavy metals, waste of sugar industry, defecation, adsorption, desorption

INTRODUCTION

Sewage of many chemical, petrochemical, electrochemical and other companies contain heavy metals which often fall into natural water bodies. Heavy metals are cumulative poisons, additive, carcinogenic and mutagenic action, so waste water containing heavy metals should be subjected to deep cleaning.

Traditionally, treatment of wastewater from heavy metals is carried by reagent and sorption methods in which expensive reagents and materials is being used which is unsustainable in terms of natural resources. At the same time in a number of industrial enterprises there are generated tonnage wastes which physicochemical properties allow to relate to the category of promising for use in water treatment. Therefore, the development of efficient and environmentally friendly ways to clean waste water containing heavy metals with use industrial waste is a challenge (Sverguzova *et al.*, 2010, 2009; Lupandina and Sverguzova, 2012).

MAIN BODY

The aim is to determine the physicochemical characteristics and the optimum process conditions of wastewater treatment from heavy metal ions (for example, Cu^{2+} and Ni^{2+}) solid waste of disaccharides production.

The objects of study were: model solutions consisting of distilled water containing ions Cu^{2+} and Ni^{2+} in concentrations of 10 and 30 mg L^{-1}, wastewater of LLC "Plant-Innovator", waste of disaccharides production-defecate of Dmitrotaranovskiy sugar factory. Chemical composition of sewage of LLC "Plant-Innovator" is presented in Table 1.

Source defecate is a loose mass of brown color. The main components of the chemical composition of the source defecate are: calcium carbonate -71% pectin -1.7%, nitrogen-free organic substances -9.5% nitrogenous organic substances 5.9%, sugar -2% calcium salts of organic acids -2.8%, minerals -3% (Sverguzova *et al.*, 2010). As the defecate composition includes organic impurities, under certain conditions of heat treatment there can be carried out combustion of organic substances to not only the final products-carbon monoxide, water and nitrogen oxides but to produce charring carbon particles deposited on the surface of the calcium carbonate, thereby forming a thermally modified defecate which have high adsorption properties. It has been suggested that the resulting thermally modified defecate must also exhibit the properties of the sorbent and it can be used for wastewater treatment.

Researches on the physical and physicochemical properties of the source and thermally modified defecate were carried out. The composition and structure of defecates point the possibility of using them for sewage treatment (Table 2).

Corresponding Author: Natalia Sergeevna Lupandina, Belgorod State Technological University Named after V.G. Shoukhov,
Kostyukov Str. 46, 308012 Belgorod, Russian Federation

Table 1: The chemical composition of the wastewater on the treatment facilities of LLC "Plant-Innovator"

Determined	The concentration of pollutants	
ingredient (units)	Before treatment	After treatment
Temperature (°C)	18.0-20.0	20-25
pH	5.2	8.2
Sulfates (mg dm^{-3})	402.5	71.3
The dry sediment (mg dm^{-3})	3000	508
Suspended solids (mg dm^{-3})	930	930
Nickel (Ni^{2+}) (mg dm^{-3})	23	0.3
Copper (Cu^{2+}) (mg dm^{-3})	12	0.1

Table 2: Physicochemical characteristics of source and thermally modified defecate

Characteristic (units)	Source defecate	Thermally modified defecate
Packed density (kg m^{-3})	1240	1320
Real density (kg m^{-3})	2710	2720
Hygroscopic moisture (%)	38.28	1.5
Melting loss (%)	37.2	32.3
Water absorption (%)	70	71.2
pH of aqueous extract	8.79	10.3
Content of CaCO$_3$ (%)	61	Up to 95
Content of organic substance (%)	Up to 20	-
Content of CaO (%)	None	Up to 5.0
Content of carbon (%)	None	0.05

As a result of the analysis, the bulk of the source defecate is 10-30 microns in size and the particles of thermally modified defecate are from 5-15 microns, i.e., during heat treatment (Sverguzova *et al.*, 2009) dispersion and specific surface area of the precursor particles increased due to destruction of the initial units because of mechanical stresses arising in steam and gas formation in the firing process of source defecate. With increasing of temperature, the mass fraction of fine particles increases. This is due to the decomposition of the calcium salts of organic acids as it previously was indicated. In this regard, it was important to determine the effect of firing temperature on the value of the specific surface of particles (Table 3).

XRD results indicate the formations of carbon charring of organic substances contained in the source defecate. The discovered carbon is similar in structure to activated coal of grade KAD. To clarify, the mechanism of the processes occurring during the firing of the original defecate, thermogravimetric studies of defecate were conducted. In this study, there were recorded such data as weight loss of the sample during the heating process, the rise of temperature during sample of Source Defecate (SD) treatment and thermal effects.

As follows from the obtained results (Fig. 1) in the temperature range from 20-110°C hygroscopic moisture is removed from the sample (curve TG), accompanied by the absorption of heat (TG portion of the curve in the same temperature range). With increasing the temperature up to 200°C there begins the process of oxidation of organic

Table 3: Changing the specific surface area of defecate with the firing temperature

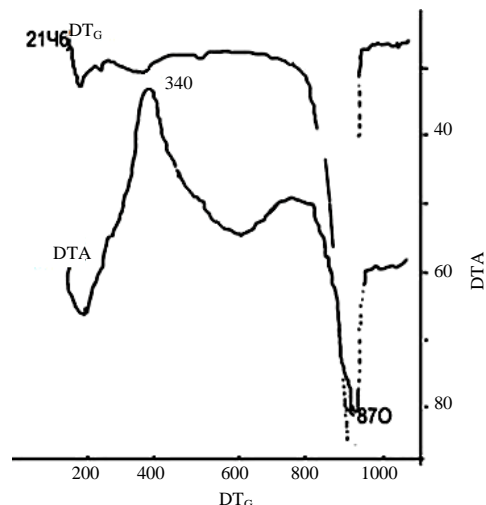| Firing temperature (°C)	Specific surface area S_{ss} (m^2/g)
Unfired defecate	54
560	71
580	72
600	73
620	74
700	76
800	79
900	83

Fig. 1: Thermogravimetric curves of source defecate: DT$_G$: Differential-Thermogravimetric curve showing in which temperature range occurs the drop in the maximum weight; DTA: curve of Differential Thermal Analysis showing in what areas occurs absorption or release of heat

substances present in the SD, it shows a small extremum on the curve TG. The process is accompanied by heat (extremum in the area DTA curve) extending to a temperature of 500°C and TG curves after temperature 340°C which corresponds to the peak on the DTA curve which characterizes the maximum heat release during the combustion of organic impurities is reduced more smoothly, it points on reducing the intensity of the process combustion of organic substances. At the temperature of about 500°C, the process of combustion of organic substances apparently stops, stopping at the stage of formation of Carbon (C) but the weight loss of the sample is not terminated, although a plot of temperatures from 500-700°C, it has a smoother nature than the interval temperatures up to 500°C. After 700°C there is a rapid process of decomposition of CaCO$_3$ as evidenced by the sharp drop in sample weight (DTG curve) and the simultaneous absorption of large amounts of heat (at least DTA). Simultaneously, with the decomposition of CaCO$_3$ carbon is completely combusted.

Therefore, the optimum firing temperature at which the carbon burnout occurs should be considered as 600°C. The studies of porous structure TD conducted by pycnometric method possible to determine the total pore volume of 0.41 cm^3/g in which the proportion of macropores is about 40%.

Thus were determined, the physicochemical properties and temperature regimes for initial processing defecate which allow its use in the process of sewage treatment.

Since, starting in the firing process the defecate charring of organic residues, formation of a layer of carbon on the surface of $CaCO_3$ as well as the decomposition of the salts of organic acids that make up the source defecate and partial dissociation of $CaCO_3$ (Lupandina and Sverguzova, 2012), we investigated the effect of the firing temperature (t_f) source defecate to treatment performance. The resulting calcium oxide alkalinizes the solution, thereby increasing the efficiency of sewage treatment due to the formation of sparingly soluble metal hydroxides (Vinogradov, 1998). The results presented in Fig. 2 show that with increasing firing temperature defecate pH of the aqueous extract is increased which leads to the formation of hydroxides.

To determine the sorptive capacity of the carbonaceous compound (Smirnov, 1982; El-Fadaly *et al.*, 2000; Abdel-Halim *et al.*, 2008) obtained in the heat treatment process, a carbonate is separated from the substrate by treatment with hydrochloric acid and subjected to infrared spectroscopy.

Analysis of the IR spectrum of carbon (Fig. 3) showed the presence of carbon double bonds of the C = C. In this case, the extraction of metals may occur by chemisorption at the place of rupture of double bonds.

To study the adsorption interaction adsorption-desorption isotherms were built for Cu^{2+} ions and Ni^{2+} (Fig. 4).

The obtained data allow us to conclude that the adsorption of metal ions has monomolecular character. Desorption occurs at low speeds and to a minor extent, it can be concluded about the nature of adsorption close to the chemical type. Adsorption energy calculations performed by the graphical method, amounted to nickel 58.2 kJ mol^{-1} and for copper, 55.7 kJ mol^{-1} which indicates the presence of specific adsorption interaction. In accordance with the theory of multilayer and polymolecular adsorption BET (Greg and Singh, 1982), ions with smaller radius are more efficient and deeply penetrating in the pores of the adsorbent, so it explains higher efficiency (98 %) of purification for ions Ni^{2+} (ion radius 78 pm) compared with the efficiency of purification (95%) of the ions Cu^{2+} (ion radius of 96 pm).
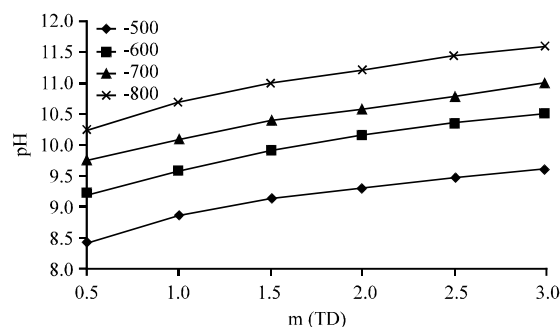

Fig. 2: Dependence of aqueous extraction pH with firing temperature of defecate
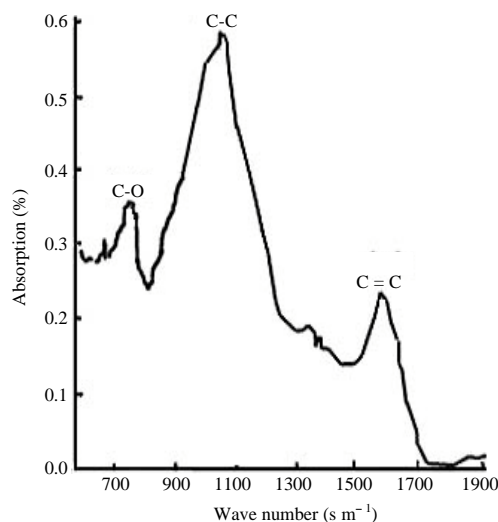

Fig. 3: IR spectrum of CTD

Figure 5-7 presents the results of investigations of the influence of various factors on the treatment efficiency of model solutions from ions Cu^{2+} and Ni^{2+} with the degree of dispersion adsorbent-reactant, mass additives TD_{600}, duration of contact of interacting substances, the temperature of the reaction medium.

Apparently by using the TD, calcined at 600°C, the driving force of the process is the adsorption which depends on the amount of carbon on the surface of the TD and the specific surface of the particles. Figure 8 presents comparative data on the effectiveness of treatment model nickel solution with various sorbents and reagents.

A similar dependence was observed for copper solutions. When used for treatment, TD, calcined at 900°C supplements weight TD_{900} is much higher. Therefore, the treatment efficiency with the addition of equal masses of TD_{600}, TD_{900}, TD_{900} is lower. From the results we can conclude that the obtained TD_{600} has high purity is close
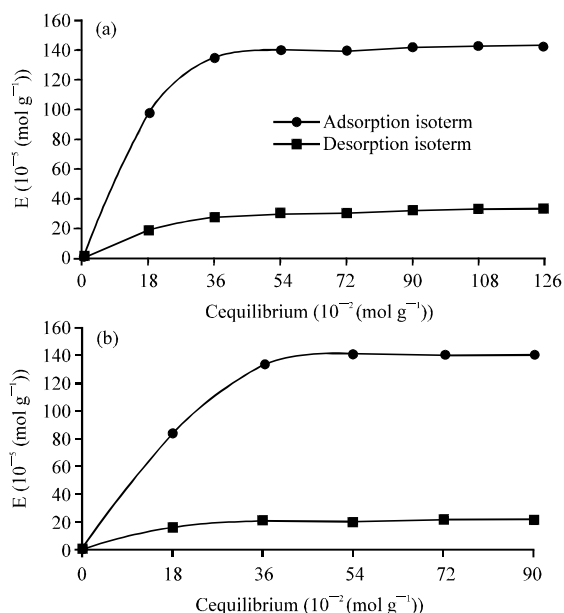
Fig. 4: Adsorption-desorption isotherms; a) ions of Ni^{2+} and b) ions of Cu^{2+} on the surface of TD (t = 20°C)
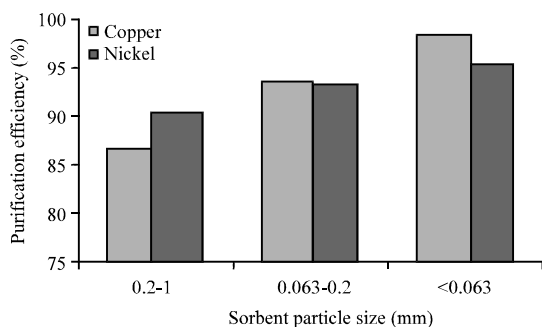

Fig. 5: Dependence of treatment efficiency with sorbent particle size, mass of sorbent 1 g/100 mL
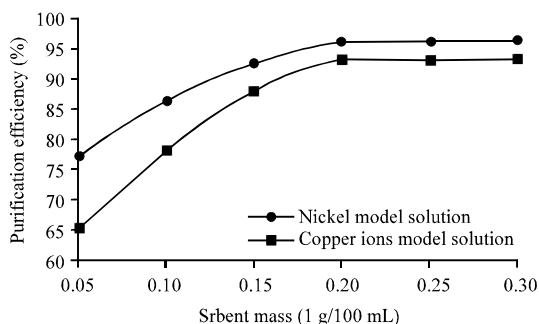

Fig. 6: Dependence of treatment efficiency with mass of added sorbent TD_{600}

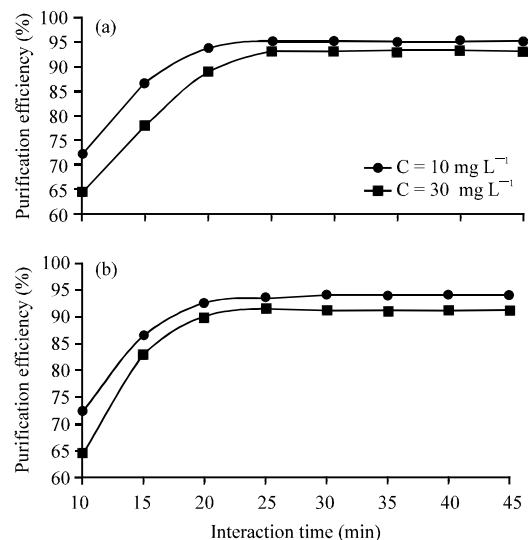in value to the purification with using KAD. This is probably due to the fact that the carbon layer in

Fig. 7: Dependence of treatment efficiency of model sewage, containing ions of nickel; a) copper and b) with time of sorbent and water contact
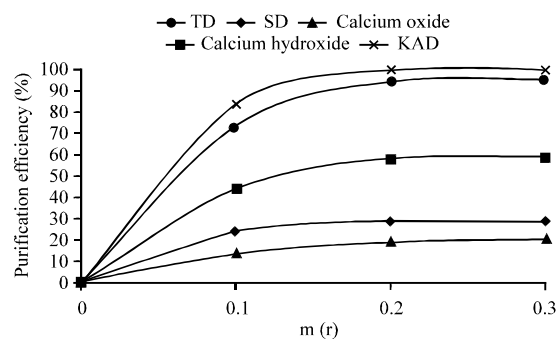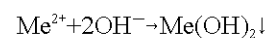

Fig. 8: The compared efficiency of solutions, containing ions of nickel, treatment with adding of different cleaning reagents (V = 100 mL, τ = 15 min, t = 20°C)

TD_{900} is absent and purification proceeds only by reactive mechanism and decreases treatment efficiency:

$$Me^{2+}+2OH^-\rightarrow Me(OH)_2\downarrow$$

where, Me^{2+}-ions of Ni^{2+}, Cu^{2+}. During the experiments, the maximum treatment efficiency using mass TD_{600} was observed at 0.2 g/100 mL of the additive solution, the duration of 25 min and mixing the aqueous medium temperature, 20°C. When we use TD_{900} the weight TD increased to 0.65 g/100 mL at the same treatment efficiency.

To clarify the mechanism of treatment solutions the change of surface [ζ] potential of TD in a solution containing ions Ni^{2+}, Cu^{2+} (Fig. 9) was investigated. It was
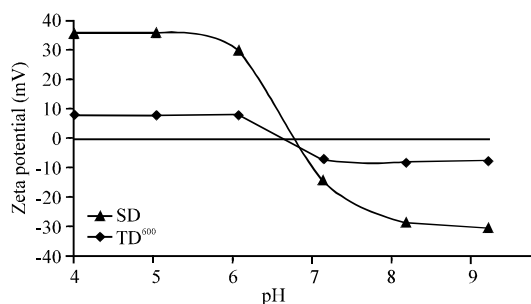
Fig. 9: Kinetics of change of [ζ] building the particle surface defecate when the pH of the medium

revealed that in acidic media with pH<4 surface of the source defecate and defecate, calcined at a temperature of 600°C has a positive [ζ] potential size, the value of which decreases with increasing pH and reaches zero at pH 6.8. This can be explained by increasing the concentration of OH^- ions in the solution and increase their share in the diffusion layer around the particles defecate. Thus, there is a complete neutralization of the particle charge defecate and coagulation of particles.

Further, increase of pH over 6.8 contributes to negative [ζ] potential on the particle surface of defecate due to the accumulation concentration of OH^- ions in solution. This should have a beneficial impact on the process wastewater from the positively charged cations of TM.

In order to determine rational parameters of the electroplating sewage treatment process of Ni^{2+} ions and Cu^{2+} there were used methods of mathematical statistics and it describes the process of sewage treatment with simultaneous exposure of several factors (Shpakov and Popov, 2003). For the mathematical description of the process there was implemented plan of the second order. The independent variables chosen were: flow of TD (m, g/LX_1), the duration of the heat treatment SD (τ, min-X_2), the interaction time (T min-X_3) and heat treatment temperature, (t, °C-X_4). Y-cleaning efficiency.

After processing the data on a computer (Fig. 10), taking into account the significance of the coefficients obtained by criteria of Student regression equation was obtained which adequately describes the process of sewage treatment from nickel ions with 99% probability:

$$Y_{(Ni)} = 82.5886+2.85784x_1-0.21128x_2+1.7236x_3+$$
$$10.24152x_4-1.8253x_{12}-1.7253x_{22}-1,52553x_{32}+$$
$$7.1747x_{42}-0.0875x_1x_2-0.6375x_1x_3+0.525x_1x_4-$$
$$0.5125x_2x_3-0.425x_2x_4+0.375x_3x_4$$

The results of regression analysis showed that 99% cleaning efficiency is attained with the following input parameters: m = 1.5 g L^{-1}; τ = 45 min; T = 15 min; t = 600°C.
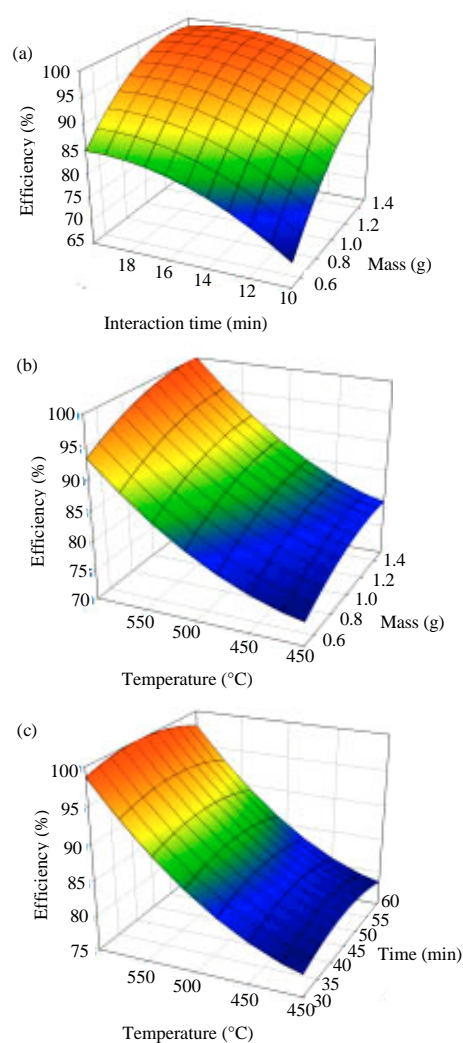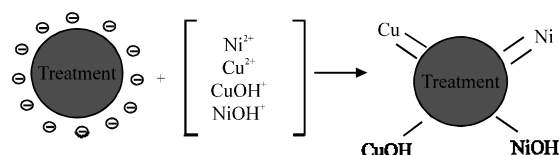

Fig. 10: Response surface in coordinates; a) temperature °C; b) the degree of purification (%) of nickel ions and c) efficiency of treatment (%)

FINDINGS

As a result of the experiments it can be assumed that the purification of model solutions may proceed simultaneously by adsorption, coagulation and reagent treatment mechanisms Adsorption mechanism:
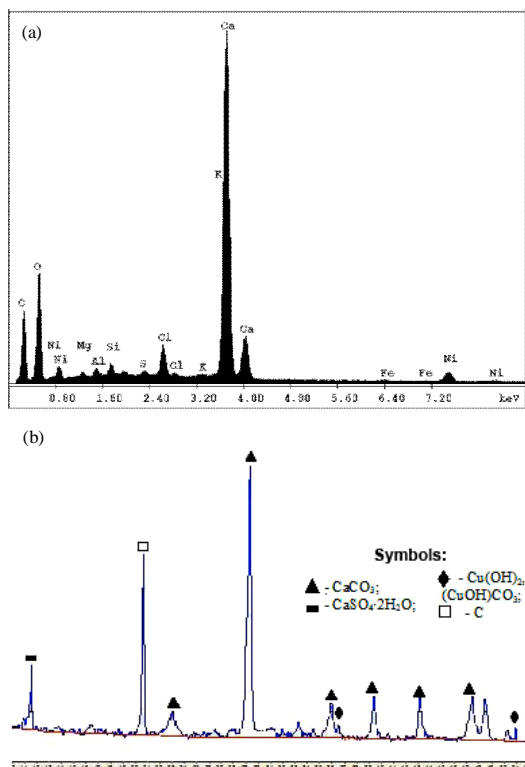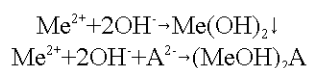

Reagent treatment mechanism:

Fig. 11: Detection of nickel and copper compounds in sediment: a) energy dispersive spectrum and b) X-ray diffraction spectrum of sewage treatment sediment

$$Me^{2+} + 2OH^- \rightarrow Me(OH)_2\downarrow$$
$$Me^{2+} + 2OH^- + A^{2-} \rightarrow (MeOH)_2A$$

where, Me^{2+}-ions of Ni^{2+}, Cu^{2+}, A^{2-}-anions. Confirmation of reagent cleaning mechanism of treatment are the results of X-ray and energy dispersive analyzes (Fig. 11) in which in the sediments of water treatment compounds Ni^{2+}, Cu^{2+} and other compounds were found.

Coagulation mechanism: Due the processes of metal ions hydrolysis occurring with an increase of pH in the solution type particles $MeOH^+$; $[Me(M_2O)_4]^{2+}$; $[Me(H_2O)_6]^{2+}$ are formed, thereby increasing the efficiency of purification of solutions (Kirovskaya, 2006).

CONCLUSION

On the base of the studies we propose the following process recommendations, the use of which allow obtaining an adsorbent-reagent that provides high quality at wastewater treatment by IHM: heat treatment temperature SD -600°C, time of heat treatment ID -30 min, weight of TD -2 g L^{-1}, the duration of interaction with the wastewater -25 min.

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