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ADSORPTION METHOD FOR ISOLATING IONS OF SOME HEAVY METALS AND PETROLEUM PRODUCTS

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ABSTRACT

The work investigated the physicochemical properties of wastewater treatment (WT) from heavy metal ions (HMI) and petroleum products (PP) using composite sorption materials (CSM), obtained from rotary slag waste from a battery plant and wood fiber waste from the city of Jizzakh, Republic of Uzbekistan. It is shown that the HMI adsorption isotherms correspond to a monomolecular layer with the participation of micro- and macropores, and it is also found that the adsorption isotherms are described by the Langmuir class of polymolecular adsorption. It was found that the efficiency of wastewater treatment from petroleum products is 90-99.6%. CSM was restored by thermal regeneration at a temperature that represents the treatment of the sorbent with steam or gases at 110°-400°C.

Keywords: wastewater treatment, heavy metal ions, petroleum products, sorption material, rotary slag, isotherms of sorption processes, Langmuir theory, environmental aspects, treatment efficiency, regeneration, heat treatment.

INTRODUCTION

Wastewater from chemical and petrochemical industries contains some heavy metal ions (HMI) and petroleum products (PP), as well as other ingredients. Such impurities, when released into water resources, cause environmental damage to a certain extent. Therefore, the study of the purification processes of WT and PP, especially the physicochemical properties of purification, is an urgent task of the time [1-4]. Currently, various methods, methods and technological installations for purifying WT impurities are used. However, a significant part of these studies are high cost, focused on imported equipment and scarce reagents. In this regard, the possibility of using rotary slag (RS) from a battery plant and wood fiber waste (WFW) has been studied [5,8,9,10].

OBJECTS AND METHODS OF RESEARCH.

It was found that the applied RS waste contains 30%-Fe(II), 15%-Na, 5.0%-Si, 2%-Pb(II) with a moisture content of 5-8% [1,6]. Based on ferritized rotary slags (RS), composite sorption materials (CSM) were synthesized with the addition of paraffin and gossypol resin with a granule size of 0.5÷3.0 mm. The elemental composition of CSM was determined using a UV-2600 X-ray fluorescence spectrophotometer from SHIMDZU, Japan, with wavelength λ = 220÷1400 nm. The presence of Fe2+ ions in RS made it possible to obtain magnetite and ferrites.

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It has been determined that at wavelengths λ=200-1400 nm, the maximum mass loss of rotary slag occurs in the temperature range t=900-1000°C and amounts to 49-58%. At the initial stage, up to a temperature of 250°C, an endothermic effect is observed, which corresponds to the region of release of crystallization water, and at temperatures above 700°C a stable phase of the starting material is formed (Table 1).

Table 1 Thermogravimetric analysis (TGA) of the original slag

Compound	Main stage of thermolysis	Weight loss in % at temperatures, °C									
	$\frac{Tn - Tk}{Tmax}$	100	250	300	400	500	600	700	800	900	1000
Rotary slag	$\frac{20 - 250}{100}$	8	28	33	40	43	49	52	5	55	58

RESULTS AND ITS DISCUSSION

To establish the nature of the adsorption purification of HMI and PP using the resulting ferritized CSM, the isotherms, thermodynamic and kinetic properties of the process were studied. At a solution temperature of 20-25°C, the amount of sorption material was 10 g/dm3, the time for establishing sorption equilibrium was 15-20 minutes. According to the BET theory, the shape of the HMI adsorption isotherm on the FFSRS surface corresponds to the formation of a monomolecular layer, with the participation of micro- and macropores (Fig. 1). Since the desorption curve is not high, in this case the sorption interaction is close to a chemical nature.

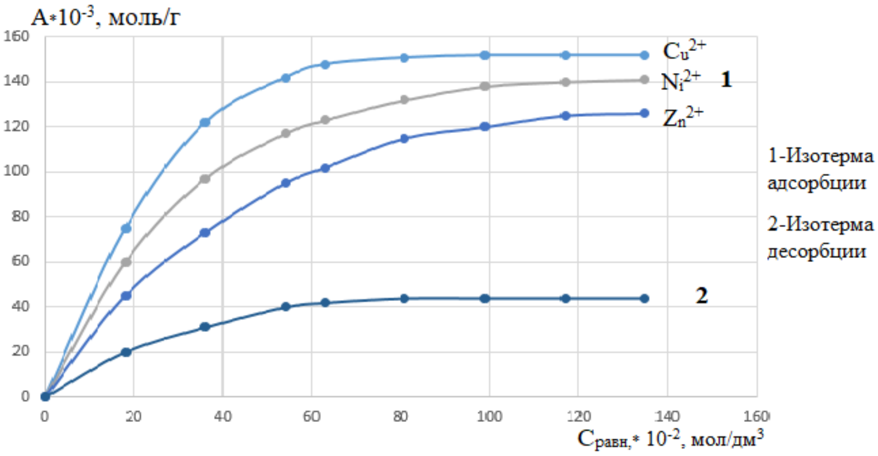

Fig. 1.- HMI adsorption isotherms using FFSRS-based CSM.

Using the method of variable portions and constant concentrations, graphs of the adsorption isotherm of PP on CSM in a neutral environment at temperatures of 298,303 and 313 were compiled. The experimental results are presented in Fig. 2. Based on the obtained adsorption isotherms, it was found that the adsorption process of PP with CSM is described by polymolecular adsorption, characteristic of porous SM (Langmuir class). At the same time, at the initial stage, the isotherms are characterized by a concave line relative to the concentration axis; as the PP content in wastewater increases, adsorption reaches saturation and leads to the formation of a plateau and the process of polymolecular adsorption until the second plateau is reached.

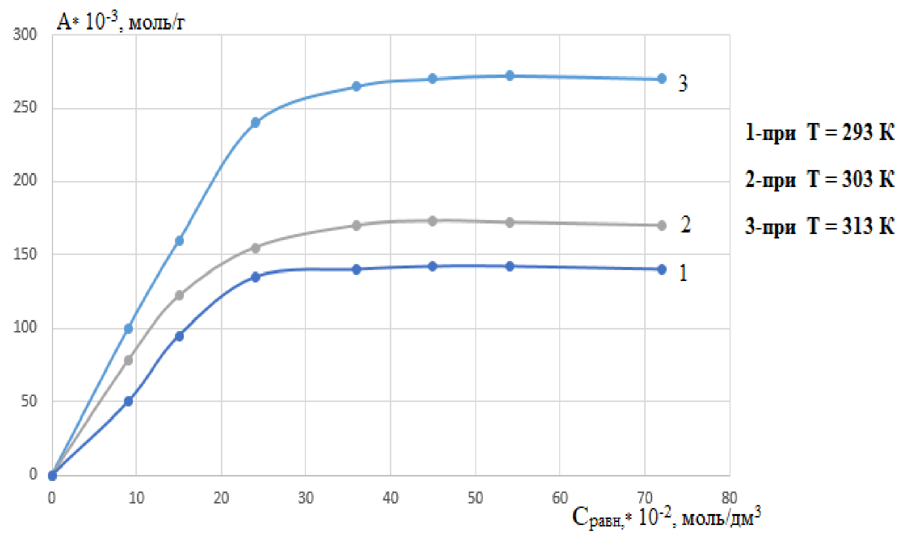

Fig. 2. HMI adsorption isotherms using CSM at different temperatures

Adsorption isotherms of PP on CSM obtained from FFSRS were processed within the framework of the Langmuir and Freundlich models. The calculations determined that in all in cases, the PP adsorption process is best described by the Langmuir model.

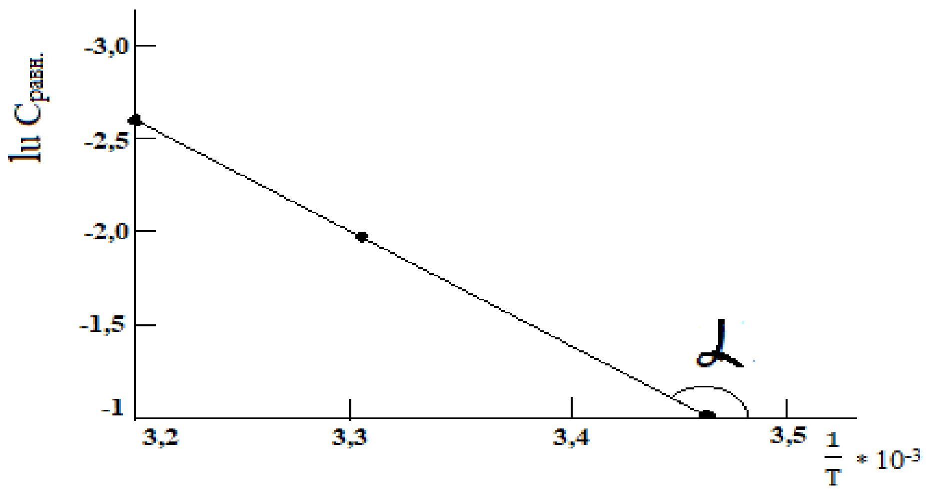

Fig. 3. Addiction ln $C_{равн.} = f(\frac{1}{T})$ for HMI.

To obtain more complete information about the mechanisms of interaction between the studied sorption material and the sorbate, the interaction energy was calculated. Dependency graphs $\ln C_{equals} = f(\frac{1}{T})$ for TM ions are shown in Fig. 3. The calculated values of adsorption energy were: ΔH_{agc}=tgɤ*R=0.0068*8.314*10³=0.05654 J/mol =56,54 kJ/mol. The calculated adsorption capacity values of CSM based on FFSRS (ferritin foul-smelling rotary slag) with respect to PP are given in Table-2.

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Table 2 Adsorption capacity of CSM based on FFSRS in relation to petroleum products under static conditions

Temperature, K	Neutral environment, pH = 6,8±0,3		Acidic environment, pH = 4,0±0,3	
	Adsorption capacity			
	Mr/r	M mol/g	mg/g	M mol/g
298	5,8 ± 0,8	0,027 ± 0,004	5,9 ± 0,08	0,028 ± 0,005
303	5,7 ± 0,8	0,032 ± 0,005	5,7 ± 0,08	0,031 ± 0,003
313	5,5 ± 0,8	0,031 ± 0,000	5,6 ± 0,08	0,030 ± 0,004

From the data in Table 2 it can be seen that an increase in temperature leads to a decrease in adsorption capacity. This course of the WT process indicates the probable physical nature of the forces holding oil products on the surface of CSM obtained on the basis of FFSRS. In an acidic environment, a decrease in the adsorption capacity of CSM with increasing temperature is also observed. All calculated thermodynamic functions have (ΔH, ΔS, ΔG) negative sign. It is known that at a negative value of the Gibbs energy (ΔG) the process proceeds spontaneously. The nature of the enthalpy of the process (ΔH) suggests that the process is exothermic. Negative process entropy value (ΔS) sorption can be explained by two factors: - since the process is exothermic in nature, i.e. when metal ions interact with FFSRS, heat is released and, from a thermodynamic point of view, entropy decreases; - with an increase in the degree of order in the FFSRS sorbent phase due to the absorption of heavy metal ions. Experimental data show that the processes of adsorption of petroleum products on CSM obtained on the basis of FFSRS belong to the processes of physical adsorption.

As a result of research, it was revealed that an increase in the degree of effect of removing petroleum products (95-99.5%) ensures the acidification of liquids containing petroleum products to pH=3-4. This is explained by the fact that the destruction of the structural-mechanical barrier occurs, i.e. destructuring of the emulsion system occurs, which more sharply reveals the difference in the magnetic properties of oil products and water, and also reduces the viscosity of the system, which in turn creates more favorable conditions for the retention of oil particles by the magnetic component of the adsorbent in a magnetic field.

After regeneration, sorption materials retain their fine crumbly structure (Fig. 4). Analysis of the considered methods, taking into account the properties of the developed CSM, made it possible to select the following regeneration methods: -thermal treatment of FFSRS after sorption of HM ions; the spent sorbent is mixed with the prepared charge of the original RS in a ratio (1:1) by weight, followed by firing in a muffle furnace at a temperature of 600- 800°C for 1-1.5 hours, which corresponds to the selected parameters of thermal ferritization; then, upon completion of the sorption process of oil and PP CSM, the absorbed substances are extracted by centrifugation or on vacuum filters.

Fig. 4. Sorption CSM using RS after regeneration (centrifugation)

CONCLUSION

Thus, the research results show that the use of magnetic CSMs together with the influence of a magnetic field on petroleum products and oil-emulsion systems during wastewater treatment contributes to a significant positive effect with appropriate design development of the devices used. Then, in the BET theory, the truss of the adsorption isotherm of HMI compounds on the CSM surface corresponds to the formation of a monomolecular layer with the participation of micro and macropores. The results of experiments on the purification of PP from wastewater under static conditions indicate the probable physical nature of the forces holding petroleum products on the surface of the CSM. In neutral and acidic environments, the adsorption capacity of FFSRS-based CSM decreases with increasing temperature. The calculated thermodynamic values of the adsorption process of PP on CSM show that this process belongs to physical adsorption.

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