

# The carbonaceous sorbent based on the secondary silica-containing material from oil extraction industry

I V Starostina<sup>1</sup>, D V Stolyarov<sup>1</sup>, Ya N Anichina<sup>1</sup> and E V Porozhnyuk<sup>1</sup>

<sup>1</sup>Belgorod State Technological University named after V G Shukhov, Kostyukova str, 46, Belgorod, 308012, Russia  
e-mail: starostinairinav@yandex.ru

**Abstract.** The object of research in this work is the silica-containing waste of oil extraction industry – the waste kieselghur (diatomite) sludge from precoat filtering units, used for the purification of vegetable oils from organic impurities. As a result of the thermal modification of the sludge, which contains up to 70% of organic impurities, a finely-dispersed low-porous carbonaceous mineral sorption material is formed. The modification of the sludge particles surface causes the substantial alteration of its physical, chemical, adsorption and structural properties – the organic matter is charred, the particle size is reduced, and on the surface of diatomite particles a carbon layer is formed, which deposits in macropores and partially occludes them. The amount of mesopores is increased, along with the specific surface of the obtained product. The optimal temperature of sludge modification is 500°C. The synthesized carbonaceous material can be used as an adsorbing agent for the purification of wastewater from heavy metal ions. The sorption capacity of Cu<sup>2+</sup> ions amounted to 14.2 mg·g<sup>-1</sup> and for Ni<sup>2+</sup> ions – 17.0 mg·g<sup>-1</sup>. The obtained values exceed the sorption capacity values of the initial kieselghur, used as a filtering charge, for the researched metal ions.

## 1. Introduction

In the present conditions of the intensive industrial production growth the problem of environmental protection against the industrial pollution becomes a more and more vital task. One of the particularly acute problems is, the generation and treatment of wastewaters, which get into the surface water bodies, pollute the subsoil and ground waters, deteriorate the water situation and complicate the water utilization [1].

The effluents of many chemical, petrochemical and machine-building industry enterprises are characterized as multicomponent ones, which contain the heavy metal compounds, oils, fats, suspended substances and petroleum products. Heavy metals are classified among the substances which have cumulative, additive, carcinogenic and mutagenic effect [2], so the waste waters, containing heavy metal compounds, are subject to fine purification. For this purpose a number of methods are used – the reagent treating methods [3], sorption methods [4], biochemical and electrochemical methods [5] and others [6]. The most preferred are sorption processes, which are highly efficient and allow using both natural [7] and artificial materials [8], as well as agricultural waste products [9, 10] and industrial waste [11].

This article presents the research findings of the use of waste kieselghur sludge (WKS) from oil extraction industry – diatomite as a feedstock for obtaining a carbonaceous sorption material.

At present, the spent kieselghur sludge is the waste belonging to hazard category 4 (low-hazardous substance) [12]. Of all the possible ways of its utilization, the most common is the above-ground



storage - over 95% are dumped on waste deposits, producing the adverse effect on the environment [13]. Besides, the inhalation of its pulverized form has a negative effect on the immunity and respiratory system [14]. So, taking into account the growing scale of vegetable oils production in Russia, the problems of enlarging the range of spent powdered sorbents application are becoming more and more relevant.

In this regard, the objective of this work is evaluating the influence of the WKS thermal modification conditions on the textural and sorption properties of the obtained carbonaceous product.

## 2. Material and methods

As an object of research the waste kieselghur sludge, generated at the stage of refined oil winterization – i.e. its fractionating by cooling, at the OAO «EFKO», Alekseevka city, Belgorod region, Russia, was considered.

The mineral composition of kieselghur sludge was studied by means of X-ray phase analysis with a diffractometer «DRON-2.0».

The microscopic study of kieselghur sludge samples was carried out by using a high-resolution scanning electron microscope «Hitach -8-800».

The thermal modification of waste kieselghur sludge was carried out by heating an averaged sample of WKS without oxygen in the SNO 25/12 electric furnace in the temperature range from 450°C to 650°C within 1 hour. The obtained product was sifted through the sieve with openings diameter 0.1 mm.

The porosity and specific surface of the native kieselguhr and the waste kieselghur sludge, thermally modified at various temperatures, were determined with a low-temperature nitrogen adsorption method by using an automated sorption unit TriStarII 3020.

The particle size of the initial and thermally modified WKS was determined by using FRITSCH Analysette 22 NanoTec Plus laser particle analyzer.

The sorption properties of the native kieselghur, used as a filter, and the thermally modified WKS were determined by their ability to absorb heavy metal ions ( $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ) in static conditions at the constant temperature (20°C) from salt test solutions. To prepare test solutions the following chemical reagents were used:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  qualified as «p.a.» (analytically pure), produced by Kyshtym copper anode plant, and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  qualified as «c.p.» (chemically pure), produced by Cherkasy chemical reagents plant. The adsorption amount for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions were determined in the concentration range of heavy metal ions from 3 to 400  $\text{mg} \cdot \text{l}^{-1}$ , the solutions volume was 50 ml, material consumption – 0.5 g, the mixing time – 24 hours. The pH value of the medium was kept within the range of 4.0 – 4.3 in order to prevent the hydrates formation process, the correction was made with HCl solution. Then the liquid was separated by centrifugation, and the concentrations of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions were determined by spectrophotometrical method using sodium diethyl dithiocarbamate and dimethyl glyoxime, respectively, with a spectrophotometer «KFK-3» according to standard techniques [15].

## 3. Results and discussion

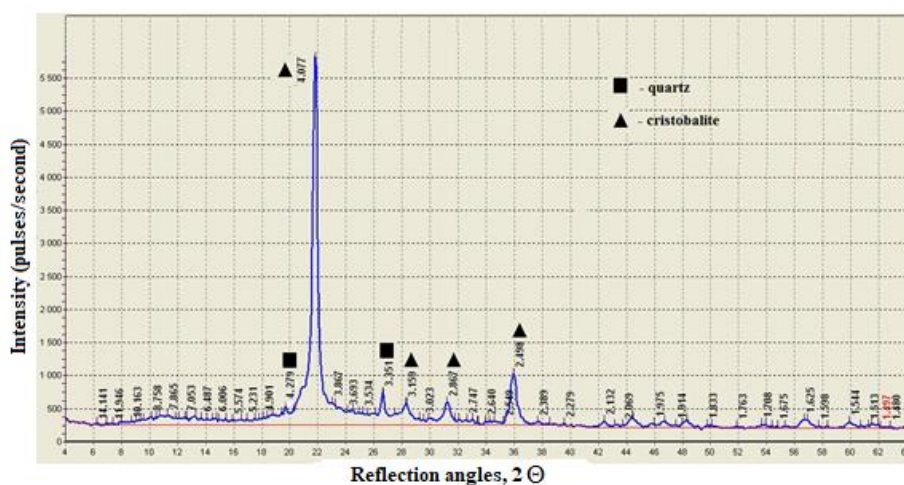
The winterization process in refined vegetable oils production implies the separation of organic impurities from the oil – the glutinous impurities and wax-like substances, which form a fine and sedimentation-stable suspension, increase the oil turbidity and make it difficult to provide the high energy and nutrient value of the product [16]. The wax-like compounds are mostly accumulated in the ground tissues of oil crops, and in the course of processing they pass to vegetable oils. The total content of organic impurities can amount to 70%, and among them the wax-like substances can make from 1.5 to 12 % [17], which depends on the species and breed of oil-bearing crops, and on the processing technology. The organic impurities are removed in precoat filtering units with the use of natural sorption materials – perlite, diatomite rocks, bleaching clay and others.

In the setting of OAO «EFKO», Alekseevka, Belgorod region, Russia, as a result of oil purification the waste kieselghur sludge (WKS) is generated, which is represented by a dingy white slow stock with 60 - 70% of fat-and-oil mixture. The mineral part of the sludge is represented by diatomite – a

light sedimentary siliciferous rock, consisting of the skeletons of microphytic diatomic algae – diatoms and radiolarians of a wide range of forms and sizes - from 10-20 nm to 0.5 mm. Taking into account the size and ordering of the pores, diatomite can be characterized as a natural macroporous material (figure 2.3). According to [18], the pores with radius of 4 – 40  $\mu\text{m}$  make about 15% of the total pore space.

As follows from the carried-out research, diatomite is mostly represented by siliceous hydrates of various water cut – varieties of opal of  $\text{mSiO}_2 \cdot n\text{H}_2\text{O}$  type, quartz impurities as a crystalline component (figure 1), which is coherent with the results, presented in the work [19]. According to the researchers [19], the diatoms' shucks appear as alternating tridymite and cristobalite layers. The opal globules are formed as early as the diatomic ooze formation stage and are registered in the diffraction pattern as an amorphous phase, namely an opal-cristobalite-tridymite phase [20].

Diatomite, which is used in the food industry as a filtering material, is thermo-chemically modified to provide its chemical inertness by means of acid treatment with the subsequent calcination at temperature 800-1000°C. This process results in the multistage removal of crystallization and adsorption water from the opaline silica and clay minerals, contained in the mineral constituent of the initial diatomite. At heating diatomite to 1000 °C the opal globules transform to cristobalite, its crystallinity degree is increased, so at studying the mineral composition of the waste kieselghur sludge under study, only cristobalite and quartz reflections are registered in the diffraction pattern (figure 1). The clay minerals, mostly represented by kaolinite, are present in the amorphized state, which is indicated by the low-intensity halo in the angular range  $2\Theta$  8-16°.

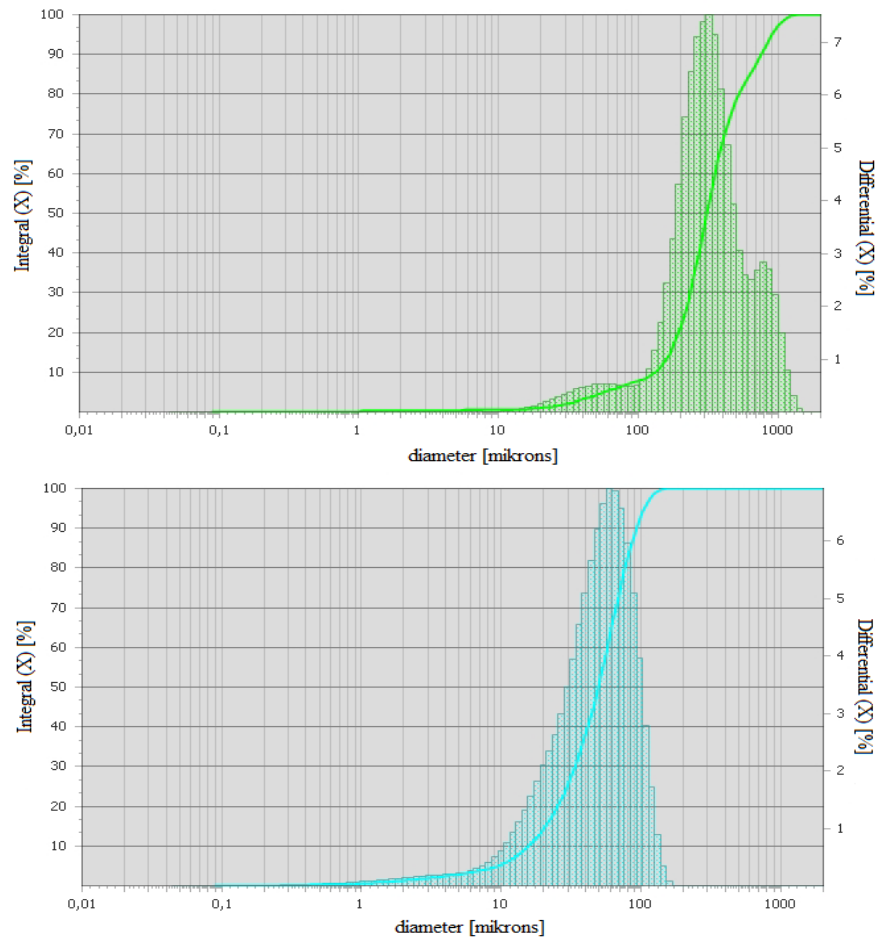


**Figure 1.** The X-ray pattern of the kieselghur sludge mineral part.

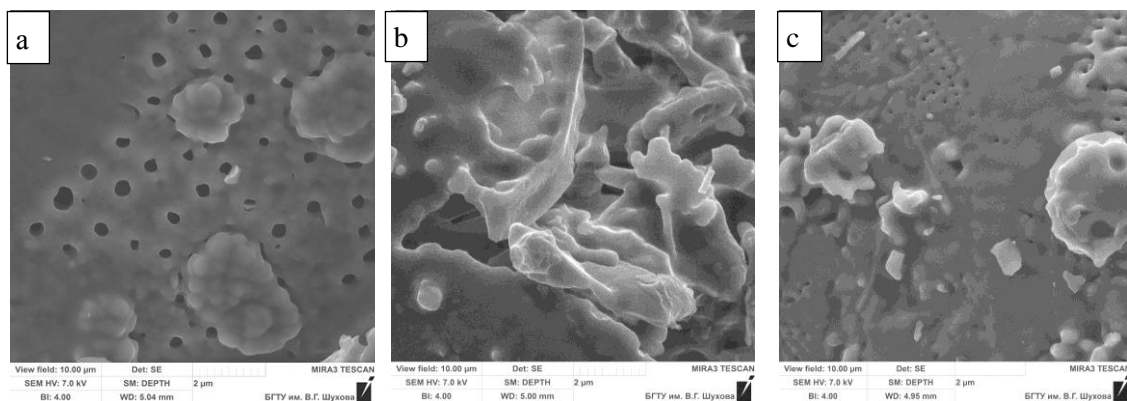
To remove the organic impurities, which pass from the purified oil to the spent sludge, and to increase its sorption activity the waste kieselghur sludge was thermally modified in the temperature range from 450 to 650°C within 1 hour. At this, the organic matter is charred, a carbon layer is formed on the surface of diatomite particles and the particle size is reduced (figure 2); as a result, a finely-dispersed product is obtained. The obtained carbonaceous mineral material was further used as an adsorbing agent to purify test solutions from  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions.

As known, the adsorption rates of various pollutants depend on a number of parameters: the properties of an adsorbing agent – its surface area, particle size and porosity, the properties and concentration of pollutants, and the conditions of the adsorption process [21, 22]. The carbon particles and other products of the organic matter oxidation, formed as a result of the WKS thermal modification, can deposit in macropores and large mesopores and occlude them. As the physical adsorption processes of diatomite are mostly provided by shucks pores and interporous areas, such processes can affect the physical, mechanical and sorption properties of the finished product. So, the

influence of the WKS thermal modification conditions on the textural and sorption properties of the obtained carbonaceous product has been studied.



**Figure 2.** The differential and integral distribution of the WKS particles (a - initial, b – thermally modified at temperature 500°C).



**Figure 3.** Results of the microscopic study of the particles: a – native (initial) kieselghur, used as a filtering material; waste kieselghur sludge, thermally modified at temperatures, °C: b – 470; c – 500.

At the low modification temperature (450-470°C) the organic matter charring process is incomplete, the products and semiproducts of the organic impurities decomposition deposit in macropores and large mesopores and «seal» or occlude them (figure 3). It results in the reduction of the obtained product specific surface - from  $2.0 \text{ m}^2 \cdot \text{g}^{-1}$  (for the native diatomite) to  $0.8 - 0.9 \text{ m}^2 \cdot \text{g}^{-1}$  (table 1).

The increase of the treatment temperature to 500°C provides the more complete organic matter oxidation, removal of semiproducts and the highest carbon particles formation. It results in the increase of the specific surface to  $3.3 \text{ m}^2 \cdot \text{g}^{-1}$  and the formation of the primarily mesoporous structure with the prevailing pores of  $15 - 79.6 \text{ nm}$  (table 1). The obtained material appears as a black finely-dispersed powder with the prevailing particles of  $55-60 \mu\text{m}$ .

The further increase of the WKS modification temperature causes the more intensive organic impurities charring up to their complete burn-off with the release of gaseous products.

**Table 1.** The influence of waste kieselghur sludge modification temperature on its textural characteristics

№	The WKS modification temperature, °C	The effective size, nm	The volume of pores less than 190 nm in diameter, $\text{cm}^3 \cdot \text{g}^{-1}$	The pore distribution relative to the total pore space, %	Specific surface, $\text{m}^2 \cdot \text{g}^{-1}$
1	Native kieselghur, used as a filtering material	15.0	0.005	20.8	$2.2 \pm 0.4$
		142.3 and more		79.2	
2		4.4		0.4	
		8.4		0.2	
		15.0		19.4	
	470	51.4	0.005	34.0	$0.9 \pm 0.2$
		79.6		0.9	
		142.3 and more		45.1	
3		15.0		25.4	
		24.0		34.0	
	500	79.6	0.005	40.6	$3.3 \pm 0.2$
4		79.6		2.6	
		142.3 and more		97.4	

The volume of mesopores is reduced, the primarily macroporous structure of the obtained adsorbent is formed, and the total pore space is reduced. Thus, at temperature 530°C mostly the pores with the effective size over 140 nm are formed, though the specific surface of the obtained product remains high –  $3.9 \text{ m}^2 \cdot \text{g}^{-1}$ , probably due to loosening of the particles as a result of vapor and gas generation.

So, as a result of waste kieselghur sludge temperature modification the finely-dispersed low-porous carbonaceous mineral materials are formed.

The waste kieselghur sludge, thermally modified at various temperatures, has been used as an adsorption material to purify test solutions from heavy metal ions by an example of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions.

The findings of studying the WKS sorption properties dependence on the modification temperature demonstrate (table 2) that the sorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions with the surface of modified sludge alters, reaching its maximum level –  $14.3 \text{ mg} \cdot \text{g}^{-1}$  and  $17.0 \text{ mg} \cdot \text{g}^{-1}$ , respectively, at temperature 500°C, which can be defined as optimal.

The findings of studying the dependence of WKS sorption properties on the modification temperature have shown that the sorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions with the surface of the modified sludge alters, reaching its maximum level at the modification temperature 500°, which can be defined as



optimal. The obtained values exceed the sorption capacity values of the initial kieselghur, used as a filtering charge.

**Table 2.** The influence of waste kieselghur sludge modification temperature on the sorption capacity of the obtained material for Ni (II) and Cu (II) ions,  $\text{mg} \cdot \text{g}^{-1}$ .

Extracted ions	Initial Kieselghur <sup>a</sup>	The temperature of WKS treatment, °C							
		450	470	500	530	550	570	600	630
Ni (II)	9.5	13.4	14.0	17.0	15.7	14.3	13.5	13.0	12.2
Cu (II)	9.12	12.2	12.8	14.3	12.2	13.2	11.8	10.9	10.4

<sup>a</sup>kieselghur, used as a filtering charge

So, the waste kieselghur sludge can be considered as a valuable organo-mineral raw stuff for obtaining carbonaceous sorption materials, which can be used in purification of wastewater from heavy metal ions.

#### 4. Conclusions

As a result of temperature modification of waste kieselghur sludge, generated at vegetable oils refining stage, a finely-dispersed low-porous carbonaceous mineral material is formed. The modification of the WKS particles surface results in the considerable alterations of its physical, chemical, adsorption and structural properties: the organic matter is charred, and on the surface of diatomite particles a carbon layer is formed, which deposits in macropores and partially occludes them. The amount of mesopores is increased, and the specific surface of the obtained product increases as well.

The optimal modification temperature is 500°C. The synthesized carbonaceous material can be used as an adsorbing agent for purifying wastewater from heavy metal ions; the maximum sorption capacity for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions is  $14.2 \text{ mg} \cdot \text{g}^{-1}$  and  $17.0 \text{ mg} \cdot \text{g}^{-1}$ , respectively. The obtained values exceed the sorption capacity values of the initial kieselghur, used as a filtering charge, for the researched metal ions.

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