Development of oil product contaminated wastewater treatment technology using sorbents based on mining waste

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Abstract. One of the most common types of ecotoxicants is oil products - unidentified group of oil hydrocarbons and products of its processing. In this regard, the development of technology for obtaining new highly efficient and inexpensive sorbents for wastewater treatment from oil products (including industrial waste) is an urgent problem. In this paper, the technology of wastewater treatment includes the use of composite sorbents based on tails-waste of Uchalinsky (UW) and Buribaevsky (BW) mining and processing plants (MPP), mica quartzite (MQ) of the Baymak field and montmorillonite clay (MC) and sodium humates (SH) obtained from waste of Tulgan brown coal. Using these sorbents, we investigated the efficiency of these sorbents in model wastewater treatment contaminated with oil from the Vozeyskoye oilfield of LLC Usinsk Neftegaz and real wastewater of "Bashneft" Ufa Oil Company. It is shown that the efficiency of treatment and the rate of adsorption of model wastewater containing oil products (8-50 mg/dm^3) increases in a number of sorbents MQ < BAU < BW (UW) + MC < BW (UW) + MC+SH (BAU is a comparison sorbent - activated carbon) and reaches a maximum for MPP coated with SH. For real wastewater containing oil products of Ufa refinery (3-625 mg/l) adsorption activity increases in the number of MQ < MQ + MC < BW + MC < UW + MC. Thus, the most effective sorbents for real and model wastewater containing oil and oil products are sorbents based on waste from Uchalinsky MPP in the composition of MH (degree of purification 96.1 %), as well as sorbent: waste UW (BW) + MC modified SH (98.1 and 98.2 %, respectively).

1 Introduction

Wastewater treatment from oil products is a serious problem for many modern enterprises of various industries (oil refining, oil, engineering, energy) [1-6].

Today there are a large number of methods of wastewater treatment from oil products with use various reagents and sorbents [7-12], many of which have a high cost and are not always effective. Therefore, it is an important and urgent task [13-15] to find inexpensive and effective sorbents for industrial wastewater treatment.

Industrial waste is one of the sources of raw materials for sorbents. Such sorbents derived from wastes of MPP and MQ [16-20], as well as montmorillonite clay (MC) [18, 19], dolomite [20] and other nonmetallic materials show high efficiency of waste water treatment from heavy metals.

The purpose of this study is to develop technology and composition of sorbents based on waste of MPP and MQ, MC and waste brown coal and investigate the effectiveness of wastewater treatment method containing oil and oil products with use these sorbents.

The objects of the study are model wastewater of oil-producing enterprises, real oil refining wastewater and sorbents based on wastes of Uchalinsky (UW) and Buribayevsky (BW) mining and processing plants, wastes of micaceous quartzite (MQ) of the Baymak field [5, 17].

2 Methods

For investigating the efficiency of treatment of model wastewater and real wastewater contaminated with oil products, we used sorbents based on waste of Uchalinsky MPP, Buribayevsky MPP, mica quartzite and clay of the Kuganak field with and without addition of humic substances, as well as the comparison sorbents of BAU. Sorbents were obtained by a method similar to [5, 17]. An obtained composition based on waste of MPP (or MQ) and MC was granulated and dried at a temperature of 100-200 ^{0}C, then it was fractionated and a fraction of 0.5-0.9 mm was selected and heat-treated of 700-900 ^{0}C. A solution of SH (mass ratio 1 %) was used to modify the surfaces of sorbents. Humates were isolated from the waste of brown coal mining by a method similar to [5, 17, and 21]. The efficiency of model wastewater treatment containing oil was studied by a stationary method [17-19].

In 100 ml of a model solution prepared from distilled water with the addition crude oil from the Vozeyskoye field of LLC Usinsk Neftegaz (Lukoil Komi) (samples N-1 and N-2), 10 g of sorbent was placed and mixed for

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Table 1. Physical and chemical characteristics of oil samples of Vozeyskoye field N-1 and N-2.

Characteristics	**oil N-1**	**oil N-2**
Gum content, wt. %	0.27	0.38
Asphaltenes, wt. %	0.36	0.43
Paraffin, wt. %	7.3	17.0
Initial boiling point,^{0}C	43	63
Boil over, vol. %:		
up to 150 ^{0}C	20.0	11.0
up to 200 ^{0}C	32.0	22.0
up to 300 ^{0}C	52.0	45.0
up to 350 ^{0}C		50.1

90-120 minutes. Water samples were taken every 10 minutes and the content of oil products was analyzed by infrared absorption in the infocolor area on the AN-3 oil product analyzer [22, 23].

Physical and chemical characteristics of oil samples N-1and N-2 are given in table 1 [24, 25].

For real refiner wastewater treatment with a concentration of 2-350 mg/l we used sorbents derived from waste of Uchalinsky MPP, Buribaevsk MPP and mica quartzite (MQ-1 - mica quartzite fraction of 0.5-0.9 mm and MQ-2 mica quartzite composition fraction of 0.05-0.1 mm and MC).

5 g of sorbent was added to 300 ml of wastewater and mixed for 90-150 minutes. Samples were taken at regular intervals and the oil content was analyzed on the AN-3 oil product analyzer.

In addition, we studied the influence of sorbent preparation temperature in the range of 700 - 900 ^{0}C on the efficiency of wastewater treatment from oil products on the example of a sorbent based on waste from Uchalinsky MPP.

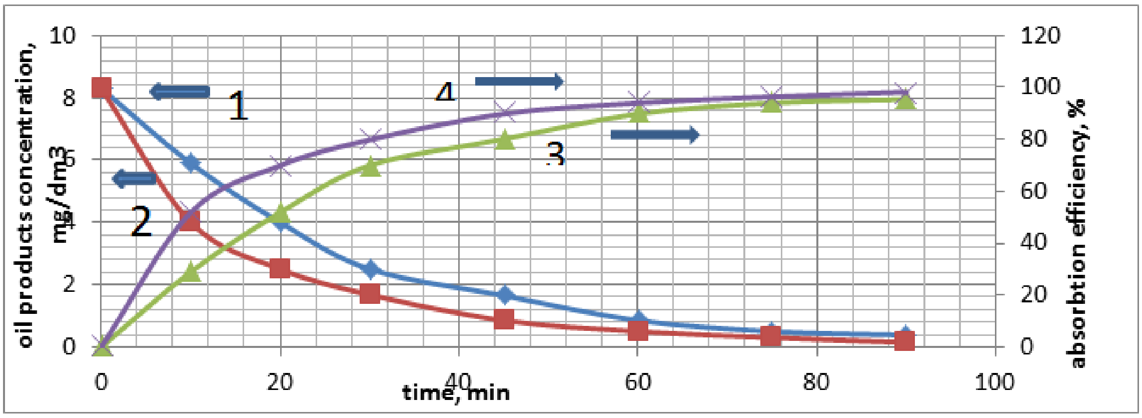

Fig. 1. Kinetic curve of pollutant concentration (1 - BW+MC and 2-BW+MC+SH sorbents) and purification efficiency (3 - BW+MC, 4-BW+MC+SH sorbent) in the process of treatment of model wastewater contaminated with N-1 oil from the Vozeyskoye field.

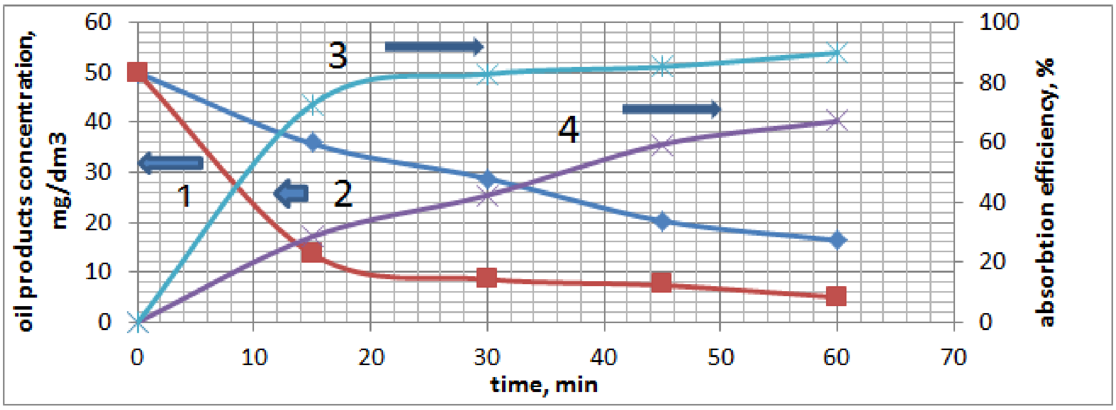

Fig. 2. Time dependence of pollutant concentration (oil of the Vozeyskoye field), (1- UW+MC+SH, 2 - BAU sorbents) and absorption efficiency (3- UW+MC+SH, 4-BAU sorbents) in the process of model wastewater treatment (N-2 oil contaminated).

Table 2. Influence of sorbent on the composition absorbtion efficiency (E) and the pseudo-first order rate constants during the waterwaste treatment from oil (the Vozeyskoye field of LLC Usinsk Neftegaz (Lukoil Komi)).

Sorbent Composition	oil sample (concentration, mg/dm^3)					
	N-1 (8.3)		N-1 (36.2)		N-2 (50)	
	efficiency E, %	rate constant $k \cdot 10^2$, min^{-1}	efficiency E, %	rate constant $k \cdot 10^{-2}$, min^{-1}	efficiency E, %	rate constant $k \cdot 10^{-2}$, min^{-1}
UW+MC						
UW+MC+SH			98.2	3.14	89.9	3.47
BW+MC	95.4	3.2	97.1	3.0		
BW+MC+SH	98.2	3.9	98.1	3.58		
BAU	64.0	2.0	83.5		67.1	1.86
MQ	40.0	0.56	60.0			

3 Results and Discussion

3.1 Study of the efficiency of wastewater treatment contaminated with oil and oil products

Tipical dependences of oil product concentration on adsorption time and treatment efficiency for model waste water contaminated with oil samples from the Vozeyskoye field (N-1 and N-2) in a stationary mode are presented in figures 1-2.

The adsorption efficiency was calculated by the formula:

$$E = \frac{(C_0 - C_t)}{C_0} \cdot 100\% \qquad (1)$$

where C_0 and C_t are the concentrations of oil products at the initial moment and the moment at.

The results of determining the maximum efficiency of model wastewater treatment contaminated with oil H-1 and H-2 sorbents based on waste of MPP, BAU, MQ, as commercial well as comparison samples of activated carbon BAU are presented in table 2.

It was shown that the modification of sodium humates solutions by sorbents based on PMM and MQ, leads to an increase in the adsorption efficiency compared to the non-modified sorbent (table 2).

3.2 Investigation of kinetic characteristic of oil adsorption

The research of kinetic characteristic of oil adsorption from model wastewater was carried out using of sorbents based on waste of MPP, mica quartzite, BAU. The dependence of the concentration of oil products on time was linearized in the coordinates adsorption equation of the pseudo first order:

$$C_0 = l_0 * e^{-kt} \quad or \quad ln\ C = ln\ C_0 - kt \qquad (2)$$

Where C_0, C_t is the initial and current concentration of oil products at time t; k is pseudo first order the rate constant of the adsorption process.

A tipical kinetic dependence of ln C for the wastewater treatment from oil (the Vozeyskoye field) using sorbents based on waste of MPP is shown in figure 3 (line1).

The dependences of the pseudo-first order rate constants of model wastewater contaminated with oil products are presented in table 2.

It should be stressed that the efficiency of treatment,

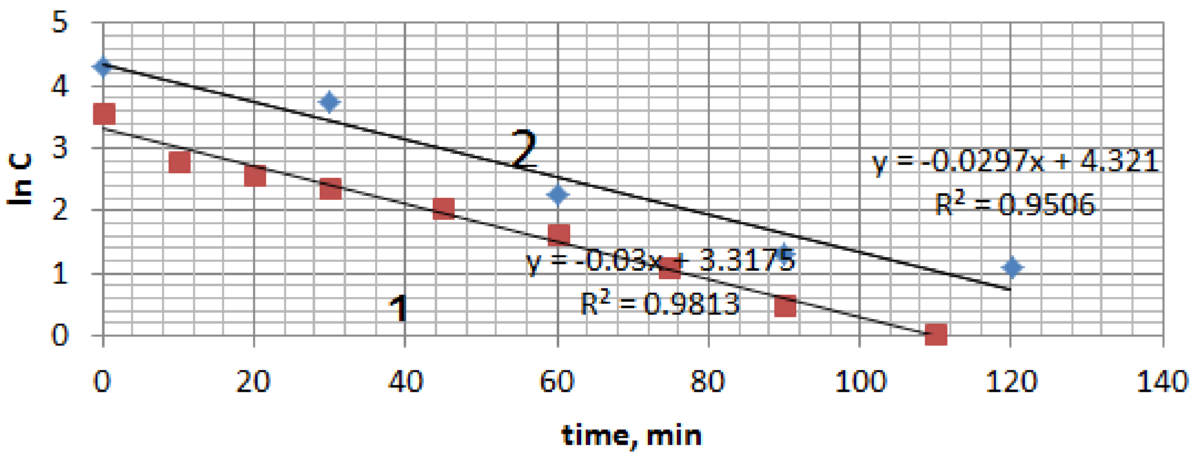

Fig. 3. Semilogarithmic kinetic dependence of pollutant concentration: 1-sorbent UW+MC-900, model waste water, contaminated by oil product, 2- sorbent BW+MC, real waste water.

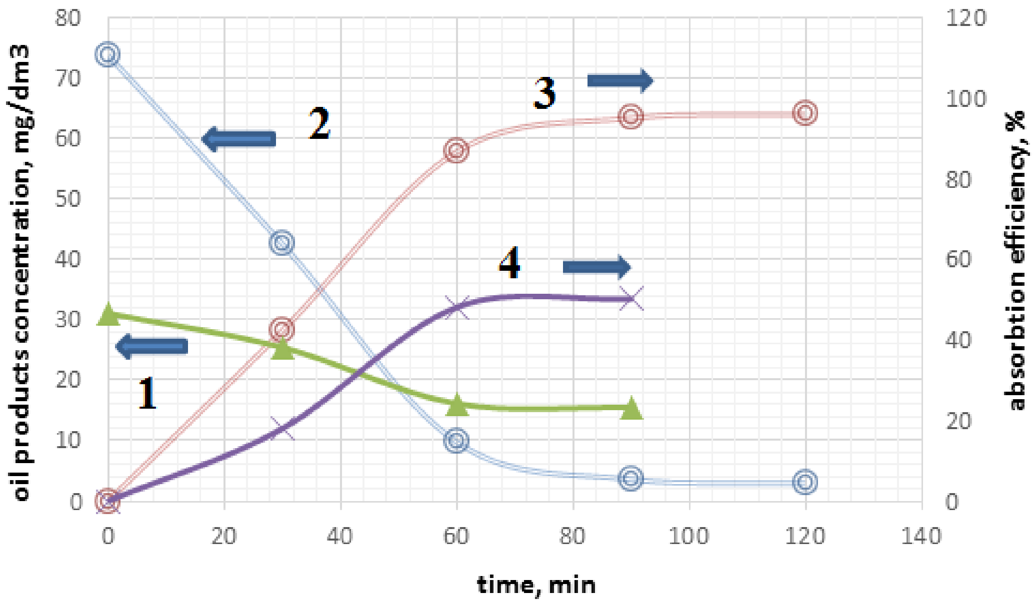

Fig. 4. Kinetic dependence of pollutant concentration (1-UW+MC, 2-MQ sorbents) and absorbtion efficiency (3-UW+MC, 4-MQ sorbents) in the process of real waster water treatment).

as well as the adsorption rate constants concurrently increase in the series: MQ < BAU < BW + MC ≈UW + MC < BW + MC+SH ≈ UW + MC+SH.

In addition, it should be noted that the model wastewater with an initial concentration of 8.3 mg / l, which is 27 times higher than the MPC for oil products in wastewater (0.3 mg/l). After application of the sorbent, the concentration is reduced to 0.15 mg / l, which is half the MPC.

Thus, sorbents from waste of Uchalinsky and Buribaevsky MPP in a composition with MC of the modified sodium humates has the greatest efficiency and also has the maximum rate of adsorption and can be recommended for further use.

3.3 Study of the efficiency of real wastewater treatment ("Bashneft" Ufa oil refinery)

In this study we used sorbents based on waste of Uchalinsky MPP, Buribayevsky MPP in the composition of MC and mica quartzite (SK-1-fraction of mica quartzite 0.5-0.9 mm and SK-2-composition of mica quartzite fractions up to 0.1 mm with MC) at a calcination temperature of 900 ^{0}C. Kinetic dependences for real wastewater treatment from oil products on the example of the "Bashneft" Ufa oil refinery are shown in figure 4 table 3.

The research of kinetic regularities of oil adsorption in real wastewater was carried out with the use of sorbents based on MPP, mica quartzite, BAU. The dependence of the concentration of oil products on time was linearzated in the adsorption equation coordinates of the pseudo-first order (see formula 1).

Tipical time dependence of ln C for the process of real wastewater treatment from oil products using sorbents based on MPP waste is shown in figure 3 (line2).

The dependences of the pseudo-first order rate constants of model wastewater contaminated with oil products are presented in table 3.

It should be noted that the efficiency of adsorption E, as well as the rate constants of the adsorption process increases in sorbent the series MQ-2 < BW + MC < MQ-1 < UW + MC (900 ^{0}C), and also increases with of growing temperature in the sequence 700 < 800 < 900 ^{0}C for sorbent UW + MC.

Table 3. Dependence of wastewater treatment efficiency from oil products (on the example of the Ufa refinery) and the rate constant of the pseudo-first order of the adsorption process on the sorbents composition.

Sorbent Composition, (temperature, ^{0}C)	concentration, mg/dm^3	efficiency E, %	rate constant $k\cdot10^2$, min^1
UW+MC (900)	73.8	96.0	2.97
UW+MC (800)	124.2	66.8	2.07
UW+MC (700)	196.5	38.9	0.37
BW+MC (900)	6.97	69.0	1.36
MQ +MC (900)	625.3	91.1	2.57
MQ (20)	46.6	50.2	0.85

Thus, the most effective sorbent for refinery wastewater treatment is mica quartzite in composition with MC and UW in composition with MC. The most effective temperature of heat treatment of sorbent is 900 ^{0}C.

4 Conclusions

1. A method of wastewater treatment from oil products have been developed using sorbents based on waste of MPP and mica quartzites modified with sodium humates, obtained from waste of brown coal mining, was developed.

2. The dependence of the efficiency and rate of adsorption on the sorbents of composition was studied.

3. It is shown that the efficiency of sorbents as well as the rate constants increases in the series: mica quartzite (MQ) < commercial activated carbon (BAU) < wastes of Buribaevsk MPP and montmorillonite clay (BW + MC) ≈ wasted of Uchalinsky MPP UW and montmorillonite clay (MC) < BW + MC sodium humates from brown coal wastes (SH) ≈ UW + MC+SH for model wastewater contaminated with oil from the Vozeyskoye field (8-50 g/l). The maximum efficiency of treatment and adsorption rate was obtained for sorbents based on wastes of Buribaevsky MPP and Uchalinsky MPP in a composition with MC and modified sodium humates E-98.2-98.1 %, respectively k = 3.1-3.6•10^{-2} min^{-1}

4. It was found that the efficiency of sorbents and the rate of adsorption increases in the sequence: MQ < BW + MC < MQ+MC < UW + MC (900 ^{0}C) for the real wastewater of the Ufa oil refinery. The highest efficiency and adsorption rate is observed for sorbents based on waste-tails Uchalinsky MPP in the composition of MC (preparation temperature 900 ^{0}C) - 96.0 % and k = 2.97•10^{-2} min^{-1}, respectively.

5. The most optimal temperature of heat treatment of sorbents is 900 ^{0}C.

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