Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. 2017. V. 60. N 6

DOI: 10.6060/tcct.2017606.5521

УДК: 502.36, 544.723.3, 628.31

РЕГЕНЕРАЦИЯ ПРИРОДНЫХ СОРБЕНТОВ, ЗАГРЯЗНЕННЫХ НЕФТЕПРОДУКТАМИ, В ПЛАЗМЕ ДИЭЛЕКТРИЧЕСКОГО БАРЬЕРНОГО РАЗРЯДА

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Работа посвящена изучению процессов восстановления сорбционных свойств диатомита, загрязненного нефтепродуктами (НП), при обработке его в диэлектрическом барьерном разряде (ДБР). Определены зависимости сорбционной ёмкости от начальной концентрации нефтепродуктов для трех видов сорбентов (диатомит, шунгит, цеолит) и установлены рабочие диапазоны концентраций НП для исследованных сорбентов. Показано, что предварительная обработка незагрязненного диатомита в ДБР приводила к увеличению его сорбционной емкости, т.е. происходила «активация» сорбента, связанная с изменением свойств его поверхности, а именно с увеличением поверхности активных центров. Максимальное число циклов регенерации сорбента в ДБР, при которых он не теряет своих физических свойств, составляет восемь циклов. Были установлены оптимальные параметры обработки загрязнённого НП диатомита в ДБР: время обработки – 1 мин, расход плазмообразующего газа – 1 л/мин, мощность, вкладываемая в разряд – 8,9 Вт/см^3. После обработки сорбента в плазмохимическом реакторе при оптимальных условиях сорбционная ёмкость диатомита увеличивается в 2,4 раза. Таким образом, по результатам проведенных исследований выявлено, что при обработке загрязненных сорбентов диэлектрический барьерный разряд обладает синергетическим эффектом: активирует поверхность сорбционного материала и приводит к деструкции нефтепродуктов, присутствующих в сорбенте, т.е. данный способ может быть эффективно использован при очистке загрязненных нефтепродуктами объектов окружающей среды.

Ключевые слова: нефтепродукты, диэлектрический барьерный разряд, сорбент, диатомит, регенерация

UDC: 502.36, 544.723.3, 628.31

REGENERATION OF NATURAL SORBENTS CONTAMINATED WITH OIL PRODUCTS IN DIELECTRIC BARRIER DISCHARGE PLASMA

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The work is devoted to the study of the recovery processes of the sorption properties of diatomite contaminated with oil products (NP) when it is processed in a dielectric barrier discharge (DBD). Dependences of the sorption capacity on the initial concentration of petroleum products (PP) for the three types of sorbents (diatomite, schungite, zeolite) were determined and working ranges of PP concentrations for the investigated sorbents were established. It was shown that pre-treatment of uncontaminated diatomite in DBP led to an increase in its sorption capacity, i.e. there was an "activation" of the sorbent, associated with a change in the properties of its surface, namely, with an increase in the surface of the active centers. The maximum number of cycles of regeneration of the sorbent in DBD, under which it does not lose its physical properties, is eight cycles. Optimum parameters of treatment of contaminated PP diatomite in DBD were established: processing time - 1 min, flow rate of plasma forming gas - 1 l / min, power input into discharge - 8.9 W/cm^3. After treatment of the sorbent in the plasma-chemical reactor under optimal conditions, the sorption capacity of diatomite increases by 2.4 times. Thus, based on the results of the conducted studies, it was revealed that when treating contaminated sorbents, the dielectric barrier discharge has a synergistic effect: activates the surface of the sorption material and leads to the destruction of oil products presenting in the sorbent, i.e. this method can be effectively used for the purification of environmentally objects polluted with oil.

Key words: oil products, dielectric barrier discharge, sorbent, diatomite, regeneration

Для цитирования:
Гусев Г.И., Гущин А.А., Гриневич В.И., Ости А.А., Извекова Т.В., Квиткова Е.Ю. Регенерация природных сорбентов, загрязненных нефтепродуктами, в плазме диэлектрического барьерного разряда. *Изв. вузов. Химия и хим. технология*. 2017. Т. 60. Вып. 6. С. 72–76.

For citation:
Gusev G.I., Gushchin A.A., Grinevich V.I., Osti A.A., Izvekova T.V., Kvitkova E.Yu. Regeneration of natural sorbents contaminated with oil products in dielectric barrier discharge plasma. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2017. V. 60. N 6. P. 72–76.

INTRODUCTION

One of the global environmental problems is the problem of pollution of water and water resources and, consequently, reduce the amount of available drinking water [1]. Problems of oil pollution aggravate more and more every year and begin to take on a global scale. Therefore, development of technologies for OP spill elimination, new technological methods for sewage purification from oil pollution becomes urgent. These methods should correspond to modern requirements – be easily accessible, convenient, environmentally friendly and economically feasible, which in particular applies to the discharge realized at atmospheric pressure [2].

Pollution of natural waters with oil products is observed almost everywhere, and their concentration varies widely. Removal of OP to values corresponding regulatory requirements is a difficult task [3].

One of the effective methods of wastewater treatment is adsorption of organic compounds which allows achieving a high degree of purification of industrial waste water [4, 5]. The advantage of this method is its effectiveness (95%), and the possibility to treat the waste water containing mixture of substances, and the recovery of these compounds [6].

The wastewater purification from hydrocarbons with DBD and ozonation is quite studied method. So, for example, in article [7] the data on purification of real wastewater from organics and heavy metals were presented under application of DBD.

One of prospective method of oil products removing at low concentrations is their destruction under the action of strong oxidants. Among them the most extended methods are ozonation and “advanced” oxidation consisting of complex impact on water with strong ecologically pure oxidants [8].

But in spite of destruction efficiency of oil products by DBD is well studied the desorption possibility of them from the sorbent surface is poorly investigated.

The objectives of this work are:

- Determination of the dependence of the sorption capacity on concentration of the solution at application of three sorbents – diatomite, zeolite and shungite;
- Determination of the optimal conditions of the sorbent regeneration process of diatomite – sorbent

processing time in the DBR, the power input to the discharge, the optimal frequency of the applied voltage and the flow rate of the plasma-forming gas;

- Determination of possible number of sorption cycles at multiple processing in the DBD.

EXPERIMENTAL

For the study we used the experimental setup for regenerating spent sorbents in DBD, a schematic representation of which is shown in Fig. 1.

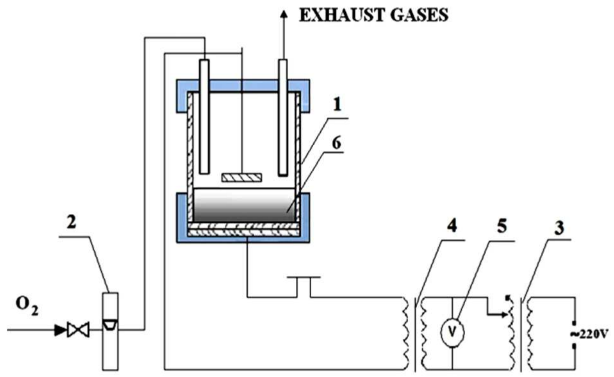

Fig. 1. The experimental setup. 1 – plasma–chemical reactor; 2 – gas flow meter; 3 – laboratory transformer; 4 – high-voltage transformer; 5 – voltmeter; 6 – sorbent

Рис. 1. Экспериментальная установка. 1 – плазмохимический реактор; 2 – газовый расходомер; 3 – лабораторный трансформатор; 4 – высоковольтный трансформатор; 5 – вольтметр; 6 – сорбент

Barrier discharge was excited by a high-voltage transformer. The magnitude of the voltage applied to the electrodes was varied in the range of 10-30 kV (used transformer allows to generate a frequency of 0.5-2.0 kHz). Control of primary voltage values was carried out by the voltmeter of D 5015 trade mark. The distance between the sorbent layer and the bare electrode during the experiments was 3 mm. Oxygen was used as a plasma-forming gas. The flow rate of carrier gas was recorded using a gas flow meter and varied from 0.2 to 2 L/min. To increase the contact surface square of the sorbent with the plasma zone the sorbent is automatically mixed.

A glass vessel of a cylindrical shape with an inner diameter of 60 mm was used as plasma-chemical reactor. The vessel was sealed with a lid made from polytetrafluoroethylene (PTFE) in which the electrode made from aluminum (∅ 30 mm) was inserted. Cover tube was also equipped with two glass pipes to supply and remove the plasma-forming gas. OP concentration was determined by fluorimetric method based on the extraction of OP from the sample by low polarity solvent (hexane) and measuring the fluorescence intensity of the extract on the device of type "Flyuorat-02" [9].

Sorbents efficiency for oil collection is firstly estimated on a value of sorption capacity on oil products [10].

The study included the contamination of different sorbents (diatomite of SMD mark, seolite of Chuguev field, shungite of Zanezhensk field) with the model solution of OP (1-450 mg/L) at dynamic conditions followed by solution treatment in DBD. In a course of experiments, the sorbent sorption capacity on OP was determined before and after treatment.

The adsorption capacity (mg/g) was calculated according to the formula:

$$J = \frac{V_0 \cdot \left(C_{0,i} - C_i\right)}{m},$$

where V_0 – volume of the solution, L; m – mass of adsorbent, mg; $C_{0,i}$ and C_i – initial and final equilibrium concentrations, mg/L.

RESULTS AND DISCUSSION

The correlation between adsorption capacity and the initial concentration OP was found for three types of sorbents: diatomite, zeolite and shungite in order to determine the operating level of contamination of the sorbent, as well as a priority object of study (Fig. 2).

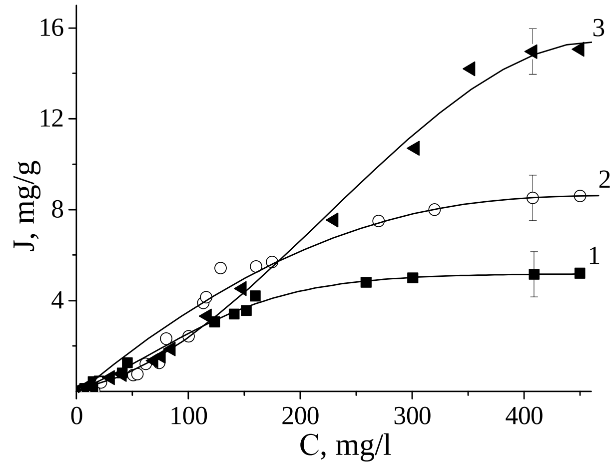

Fig. 2. Dependence of sorption capacity on the initial concentration of OP (1 – shungite; 2 – zeolite; 3 – diatomite)

Рис. 2. Зависимость сорбционной емкости от начальной концентрации НП (1 – шунгит, 2 – цеолит, 3 – диатомит)

The results show that the most effective sorbent is diatomite since its sorption capacity in the tested concentration range of oil does not reach the saturation limit. For zeolite and shungite the increase in concentration of oil in the solution in the range of 250-406 mg/L does not cause a significant change in adsorption capacity. The evaluation of sorption properties included prior pollution of initial sorbent by model OP solution (to create a model solution the engine oil

M8-B was used) by passing 100 mL of the model solution. An working concentration of the OP in the solution was 70 mg/L. The dependence of the sorption capacity of diatomite treated with the discharge on power inputted to the discharge is shown in Fig. 3.

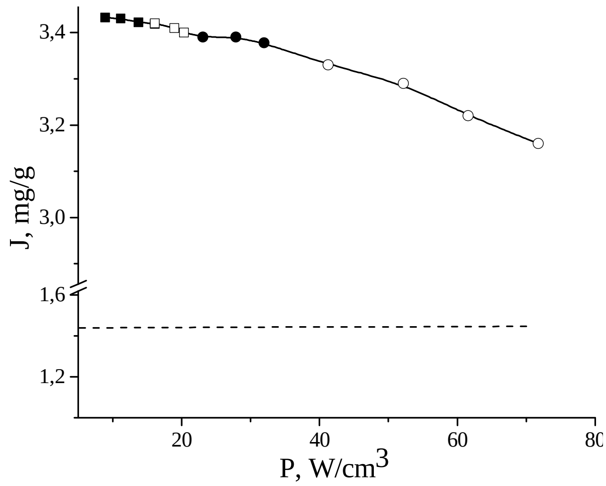

Fig. 3. The dependence of the sorption capacity of the diatomite treated by OP on the value of the power inputted to the discharge (treatment conditions: the plasma gas flow rate - 1 liter/min, processing time –1 min ■ – 0.5 kHz; □ – 0.8 kHz; ● – 1.5 kHz; ○ – 2.0 kHz; --- – the initial sorption capacity)

Рис. 3. Зависимость сорбционной емкости диатомита, содержащего НП, от величины мощности, вкладываемой в разряд (условия обработки: расход плазмообразующего газа – 1 л/мин. Время обработки –1 мин; ■ – 0,5 кГц; □ – 0,8 кГц; ● – 1,5 кГц; ○ – 2,0 кГц; --- – начальная сорбционная емкость)

The data presented in Fig. 3 show after the treatment of the sorbent in plasma chemical reactor, diatomite's sorption capacity is increased by a factor of 2.4, i.e. sorbent modification occurs that causes a change in the surface properties and likely implies the increase in the concentration of active centers. At increasing in the power inputted to the discharge, as well as at change in the frequency of the applied voltage the sorption capacity of sorbent insignificantly reduced, which may be associated with combustion of particles created at high voltages. Due to combustion the cooling of the surface layers due to adsorption of heat of the endothermic reactions on the sample surface and in the surface pores (with micro pores burnout to medium and macro sizes) [11]. Optimum power deposited to the discharge at which the diatomite modification occurs was 8.9 W/cm^3 (0.5 kHz AC frequency).

The dependence of the sorption capacity of the spent sorbent by OP on the processing time is shown in fig. 4. With the increase of treatment time from 1 to 5 min, sorption capacity remains unchanged, and with further change in time it decreases insignificantly from 3.4 to 3.2 mg/g.

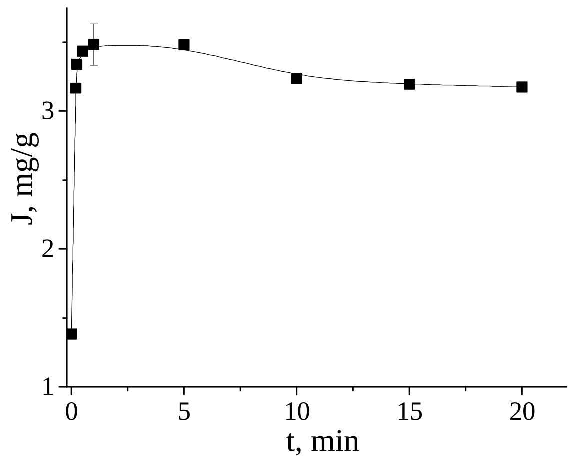

Fig. 4. The dependence of the sorption capacity of the diatomite treated by OP on the processing time (treatment conditions: the power deposited to the discharge – 0.18 kW, plasma gas flow rate - 1 L/min, the frequency of the applied voltage - 0.5 kHz)

Рис. 4. Зависимость сорбционной емкости диатомита, содержащего НП, от времени обработки (условия обработки: мощность, отводимая на разряд - 0,18 кВт, расход газа плазменного потока - 1 л/мин, частота приложенного напряжения - 0,5 кГц)

Thus, the optimal processing time for restoring contaminated diatomite of its sorption properties is 1 min.

Study of the dependence of adsorption capacity of sorbent treated by OP on the volumetric flow rate of the plasma-forming gas showed that the increase in the gas flow from 1 L/min to 2 L/min results in a slight decrease of the sorption capacity. This is probably due to the carryover of the active particles generated in the discharge. Thus, optimum plasma gas flow is 1 L/min.

To evaluate the number of cycles of "sorption-desorption" of adsorbent under study experiments were conducted at multiple treatments in the DBD (table).

It was found that at the regeneration of contaminated adsorbent its sorption properties decreased. However, even with the maximum number of regeneration cycles sorption capacity decreased by 1.4 times as compared with the activated adsorbent, but it does not reach the magnitude of sorption capacity typical for initial diatomite (1.44 mg/g).

Table 1

The dependence of the sorption capacity on the number of sorption/desorption cycles

***Таблица*. Зависимость сорбционной емкости от числа циклов сорбции/десорбции**

№ Cycle	The initial sorption capacity	1	2	3	4	5	6	7	8
Indicator adsorption capacity of the sorbent, mg/g	1.4	3.4	3.32	3.3	3.2	3.2	3.0	2.7	2.4

The results obtained allow making conclusion on possibility of multiple regeneration of adsorbent with the maintenance of its sorption properties which are necessary for sewage treatment from petroleum products.

CONCLUSION

Research has shown that treatment in DBD uncontaminated OP diatomite increases sorption capacity. This means that in addition to adsorbent regeneration in DBD, the surface modification occurs which causes an increase in the surface activity of diatomite. Variation of different processing parameters (power deposited to the discharge, time of the treatment, the carrier gas flow rate) results in a slight decrease in adsorption capacity. The estimation of the number of possible sorbent regeneration cycles showed that the sorption capacity decreases with each cycle, but even on the eighth cycle the sorption capacity of processed diatomite is higher than of initial 1.4 times.

Acknowledgements. *This study was supported by Ministry of Education and Science of the Russian Federation (the project № 4.1385.2014/К).*

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Поступила в редакцию 29.12.2016
Принята к опубликованию 18.04.2017

Received 29.12.2016
Accepted 18.04.2017