Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

ISSN: 0972-6268	Vol. 14	No. 3	pp. 685-690	2015

Original Research Paper

Purification of Industrial Enterprises Wastewater from Petroleum Products Using New Granular Hydrophobic Sorbents

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com
Received: 4-11-2014
Accepted: 19-1-2015

Key Words:
Industrial wastewater
Hydrophobic sorbents
Kazan CHP-1
Water purification

ABSTRACT

The authors propose to use the dried carbonate sludge of chemical water purification (CWP), Kazan CHP-1 as a sorbent of petroleum products. Oil capacity was assessed by its ratio to the most distributed TPS oil products in the wastewater: turbine oil, diesel fuel, gasoline, reduced fuel oil, and oil of the Shiiskoe deposit. The result of the studies show that, one of the disadvantages of the sludge as an oil product sorbent is its hydrophilicity. To obtain a hydrophobic sorbent as a slurry modifier, the GKZh-94M water repellent organic silicon liquid was used (136-157M, TU 6-02-691-76). To impart water-repellent properties to the sludge, its surface is hydrophobized. At hydrophobic treatment, the sorption capacity is increased 2.5-fold relative to the starting sludge. When using a hydrophobic finely dispersed sludge in dry bulk, a number of problems arise viz., there is a hydrophobic "plug", and wall surface effect of the fluid flow occurs. It is possible to avoid these problems and to use the maximum sorption capacity of hydrophobic sludge in dry bulk filter by decreasing the bulk density, i.e. forming granules. Volumetric and surface hydrophobization of granules was investigated. Study was conducted to determine the effectiveness of purification of sorbents in the dynamic conditions, simulating the industrial adsorption filter. Purification efficiency was more than 98% and the concentration of petroleum products in the permeate was less than 0.1 mg/dm^3. We investigated the physical and mechanical properties of local soils with the addition of waste sorbents. According to the results of the research, there is a beneficial effect of introducing a waste sorbent as a modifier in the fortified ground, consisting in the growth of frost resistance and tensile strength in bending.

INTRODUCTION

Nowadays, in the home energetics, there is a tendency of the transformation of thermoelectric power stations to an environmental friendly and drainless technology. A significant reduction in the amount of TPS wastewater, the recycling industrial wastes and their returning to the technological cycle of the station, the water coolant multiple usage, and the recycling saline solutions are the main directions to achieve ecological security.

Storage of wastes and increase of their quantity is becoming a growing problem in the industry these days. Currently, the researches in the field of the waste recycling are being actively done viz., the allocation of valuable components and their recycling in the production cycle of the enterprise. This paper describes a technology for the recycling of TPS water installation wastes-carbonate sludge for the needs of the station and the reduction in the amount of warehousing.

Water polluted by oil products has a significant impact on the environment. Among the most effective ways of wastewater purification with low concentrations of petroleum products, is adsorption.

MATERIALS AND METHODS

The authors propose to use the dried carbonate sludge of chemical water purification (CWP) Kazan CHP-1 as a sorbent of petroleum products. The CWP TPS illuminator sludge is a lime-treatment and coagulation product, a natural raw-material and a stable mixture of a certain chemical compounds (Gromoglasov et al. 1990). The composition and the component ratio of the sludge depends on the chemical composition of the raw water. The ash content of the sludge is 89%, organic carbon 11% and humic acid up to 12 %. The sludge is characterized by finely dispersed composition, and the presence of the polar functional groups of the humic substances on its surface (Nikolaeva et al. 2011a).

In the works (Nikolaeva et al. 2010a, Nikolaeva et al. 2010b) on the assessment of the sludge efficiency as an oil product sorbent, its oil capacity, moisture capacity and fluidity were determined experimentally. The oil capacity was assessed by its ratio to the most distributed TPS oil products in the wastewater viz., turbine oil, diesel fuel, gasoline, reduced fuel oil and oil of the Shiiskoe deposit. The results of studying the kinetics of the absorption process by the weight method, in conditions where a sludge sample was submerged in pure oil product samples, show that the sorption capacity of the sludge is achieved in the first minutes of contact with wastewater; after 25 min, it reaches 0.5-0.7 g/g for turbine oil, diesel fuel and gasoline, and 1.5 g/g for reduced fuel oil, which constitutes 50-70 and 150%. As well, later, it does not increase, which speaks of the onset of sorption equilibrium (Nikolaeva et al. 2010b). In this case, the relation of sorption characteristics of petroleum products is in proportion to their viscosity.

Sludge moisture capacity is 57.13%, the buoyancy 1.2% and the size of middle fraction 0.09-1.5 mm. According to the received data, we can judge that the sludge without the additional processing has a low adsorption capacity in relation to petroleum products, a high dispersity and hydrophobicity.

The result of the studies show that, one of the disadvantages of the sludge as an oil product sorbent is its hydrophilicity. To impart water-repellent properties to the sludge, its surface is hydrophobized. As a hydrophobizator, having a good water vapour permeability, various chemical substances, predominantly organosilicon, are used (Kamen'shchikov & Bogomol'nyi 2005). To obtain a hydrophobic sorbent as a slurry modifier, the GKZh-94M water repellent organic silicon liquid was used (136-157M, TU 6-02-691-76). The active hydrogen content of $CH_3(SiHO)_n$, where n = 10-15, reaches 1.5-1.8wt %. Kinematic viscosity at 20°C is 1.5×10^{-5} m^2/s, and the water extract pH is 6-7. To obtain the sorbent, the sludge is mixed in a L/S (liquid to solid) volumetric ratio of (0.3-0.6):1 with a water emulsion of polymethyl hydrosiloxane (2% solution) (Nikolaeva & Golubchikov 2011b).

For a comparative assessment of the sorption capacity of the initial (curve 1, Fig. 1) and modified sludge (curve 2, Fig. 1), tests on absorption of Shiiskoe deposit oil were conducted. The sorption capacity of the sludge increased by 10%. This is explained by the lower apparent density, $ñ_a$ and partial swelling of the water-repellent modified sorbent. By varying the temperature and treatment time, the optimal conditions were determined for obtaining a water-repellent sorbent; the dry-weight sorbent (50 g) of the 0.01-1.40 mm fraction (0.01-0.09 mm, 30%; 0.09-1.40 mm, 60%; 1.4 mm »10%) was treated with 12.5 mL of an 8% water emulsion of polymethyl hydrosiloxane (GKZh-94M) at a volumetric ratio of L/S= 0.25 : 1. The mixture was carefully stirred, placed in a muffle furnace, heated to 410°C, and held at this temperature for 9 min. Then the modified material was taken out and cooled in the air. The sorbent became friable, and the apparent density was 736 kg/m^3. The sorption capacity increased by 65-70% depending on the time of contact between the sorbent and oil products (curve 3, Fig. 1). This is explained by the fact that the majority of low molecular organic admixtures decompose at a temperature of 200-300°C. The main quantity of gaseous products in the decomposition of the sludge and GKZh94M (CO_2, CO, CH_4, etc.) form at a temperature of 350-600°C. As well, intense carbonization of the sorbent proceeds. At this stage, partial aeration and oxidation of the sorbent and complete oxidation of carbon to CO_2 occur, as a result of which the sludge takes on a developed porous structure. At the heat treatment temperature of 900°C complete decomposition of poly-

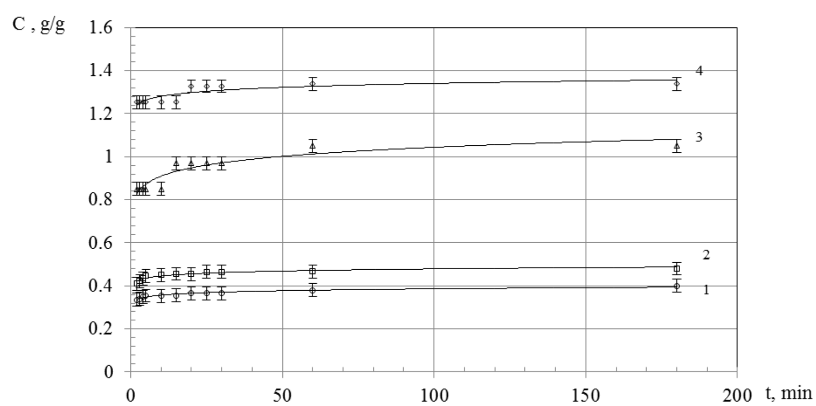

Fig. 1: The sorption capacity of modified sorbents in relation to oil.
1 - Source sludge; 2 - Sludge, treated with GKZh - 94M, without heat treatment; 3 - Sludge, treated with GKZh - 94M, heat treatment at (400 ... 420)°C; 4 - Sludge, treated with GKZh - 94M, expanded at 900°C.

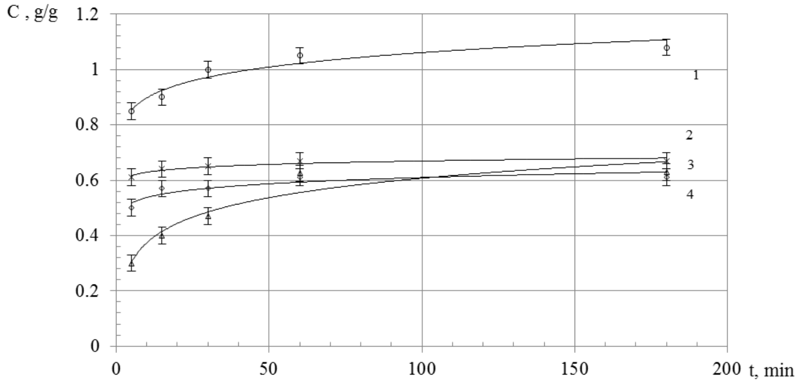

Fig. 2: The sorption capacity for oil sludge modified by different hydrophobizing.
1 - GKZh - 94M, 2 - EK WS 100, 3 - liquid sodium glass, 4 - NeoMID WaterSTOP Bio

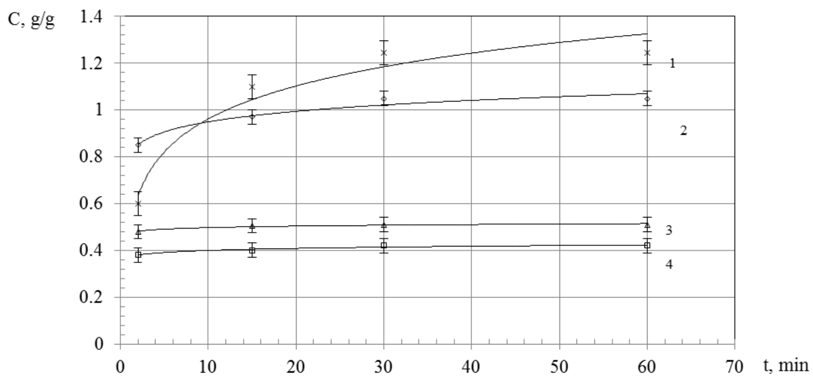

Fig. 3: The sorption capacity of “Sorbent-1”, “Sorbent-3” to relation to gasoline AI-92 and Shiiskoe deposit oil.
1- oil “Sorbent-3”, 2 - oil “Sorbent-1”, 3 - gasoline AI-92 “Sorbent-3”, 4 - gasoline AI-92 “Sorbent-1”.

methyl hydrosiloxane occurs, sludge in admixture with the decomposition products of GKZh-94 has a low bulk density (»300 kg/m^3), and completely loses its hydrophobic properties after which reprocessing of the hydrophobizing composition (curve 4, Fig. 1) is required (Nikolaeva & Golubchikov 2012a).

The graphs, show that at hydrophobic treatment the sorption capacity increased 2.5-fold relative to the starting sludge.

To compare the efficacy of hydrophobization sludge processing with hydrophobic compounds GKZh-94M, EK WS 100, NeoMID WaterSTOP Bio, liquid sodium glass GOST 13078-81 was carried out. Processing was carried out with the same concentration of emulsions L/S - 0.25:1 and temperature of 410°C for 9 minutes.

The determination of the sorption capacity of the sorbents was carried out in relation to Shiiskoe deposit oil. Measurements were carried by the gravimetric method (Nikolaeva & Golubchikov 2011c). The results are presented in Fig. 2.

The most effective is hydrophobizing composition GKZh - 94M (curve 1, Fig. 2), the sorbent is obtained on its basis, further has the name “Sorbent-1.”

When using a hydrophobic finely dispersed sludge in dry bulk filters, the number of problems arise:

a. A hydrophobic layer on the surface of the sludge has the wetting angle over 90°C. In this case, there is a hydrophobic “plug”, blocking the flow of water at the atmospheric pressure.
b. Feeding a flow of water on the hydrophobic finely dispersed sludge under the pressure arises wall surface effect of the fluid flow occurs (Nikolaeva & Golubchikov 2011d).

It is possible to avoid these problems and to use the maximum sorption capacity of hydrophobic sludge in dry

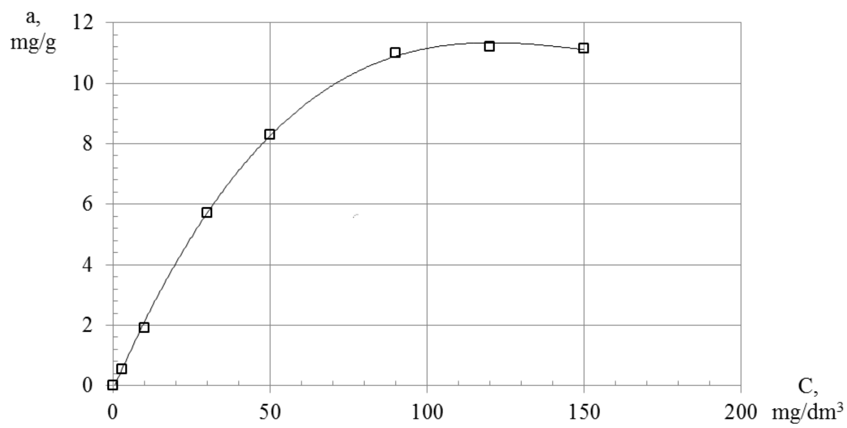

Fig. 4: The adsorption isotherm of “Sorbent-5” petroleum products out of the water under dynamic conditions.

bulk filter by decreasing the bulk density, i.e. forming granules. The sludge treated with liquid sodium glass during the heat treatment forms into granules by pelletizing with a certain degree of durability, since the under long heat treatment, the molecular structure of the liquid glass transforms into a crystal lattice (Korneev & Danilov 1996).

To receive polydisperse granules (0.01 ... 0.09) mm the sludge was mixed with sodium waterglass in a ratio of 2:1. This ratio was optimal and optimized experimentally. The obtained granules have a diameter of the sorbent particles (0.5 ... 5) mm, abrasion number-78%, high hydrophilicity, and pH of water extract-10.2. When flushing, pH of the filtrate was restored to neutral 7-7.5 (Nikolaeva et al. 2012b).

To obtain granules, having water repellent properties is necessary for hydrophobization. Volumetric and surface hydrophobization was investigated (Sobolevskii et al. 1975). At a volumetric hydrophobization, hydrophobizing composition is introduced into the mass of the material together with a plasticizer, when the superficial one, heat-treated granules are a impregnated emulsion hydrophobizator.

For carrying out volumetric hydrophobization, the emulsion of sodium waterglass and GKZh-94M in the ratio of 1:1 is prepared. To obtain granules having water repellency, finely dispersed sludge (0.01 ... 0.09) mm is mixed with the mixture in the ratio of 1:2 to full impregnation of the material. Further, the formation of granules is carried out by pelletizing. The obtained granules are heat treated at 250°C before the establishment of constant mass. Then, the sorbent is placed in a desiccator, where it is cooled to room temperature (Nikolaeva & Golubchikov 2013). The obtained sorbent has the abbreviation “Sorbent-3”. The middle size of the granules of the sorbent is (0.5 ... 2.5) mm, abrasion number-65%, a total pore volume-0.31 cm^3/g, a porosity-76.3%, buoyancy-97.5%, and moisture capacity-1.6%.

The values of the sorption capacity “Sorbent-1”, “Sorbent-3” in relation to gasoline AI-92, Shiiskoe deposit oil are experimentally determined and shown for comparison in Fig. 3.

The results show that the sorption capacity “Sorbent-3” (curve 1, 3, Fig. 3) exceeds the capacity of “Sorbent-1” (curve 2, 4, Fig. 3) to (15 ... 20)%. The granules “Sorbent-3” have a high retention capacity, as the given sorbent is characterized by the porous structure.

To assess the effectiveness of the “Sorbent-3”, the purification of the wastewater polluted with oil products in dynamic conditions was done. For the experiment, the filter glass column of 2.5cm diameter was used. A series of experiments with changes in height of the sorbent loading from 5 to 35 in steps of 5cm were carried out. Then, through a layer of sorbent load, wastewater was passed. The water amount was 500 mL and filtering rate was 3.5 m/h. The filtrate was analysed for the residual concentration of petroleum products. The determination of the mass of oil product concentration in the filtrate was carried out with IR spectroscopic method on the device AN-2 [GOST R 51797-2001].

To carry out a superficial hydrophobization, the granules of the sludge were processed with the emulsion of hydrophobizator of a certain concentration. As water repellents GKZh-11n, GKZh-94M, organosilicone fluid “Silor” were used.

The research on the dependence of porous structure, the total pore amount of the pellet sludge on processing temperatures was done. The treatment temperature was varied from 200°C to 800°C. At the heat treatment temperature of 700°C reached its maximum value of the total pore volume -0.56 cm^3/g and porosity-81%. As a result, the sorption capacity for gasoline AI-92 reached 0.7 g/g.

Temperature of 700°C is selected as optimal. At this temperature, the moisture is completely removed, including the related decomposition of organic substances. When allocating, degradation products formed a developed porous structure, and there is an increase of the specific surface.

To give hydrophobic effect, during a surface treatment of sludge, the granules obtained at 700°C impregnated aqueous emulsions of different concentrations of water-repellent material.

We experimentally determined optimal concentrations of hydrophobizator as 5% in an aqueous solution of GKZh-94M, close to optimal. While applying a polymer liquid on the surface at a concentration of impregnation from 5% to 10%, there was a decrease of the total pore amount of 28% compared with granules without impregnation, and will not be further decreased. At impregnation, the granules of sludge emulsion at a concentration greater than 10% total pore volume is not changed. This confirms that the excess of the hydrophobizator does not remain on the surface and passes into the filtrate (Nikolaeva et al. 2012b).

The granules were impregnated with a solution of the hydrophobizator and heat treated at 150°C for 60 minutes. This sorbent is referred "Sorbent-5". The obtained sorbent has a bulk density of 0.536 g/cm^3, a total pore volume of 0.57 cm^3/g, a porosity of 80.72%, average granule size of (0.5 ... 1.6) mm, abrasion number of 68% , moisture capacity of 0.9%, buoyancy of 99%, and the sorption capacity in relation to gasoline AI-92-0.67 g/g.

The experiments conducted, determined the effectiveness of purification in the dynamic conditions simulating the industrial adsorption filter. Purification efficiency was more than 98%, and the concentration of petroleum products in the permeate less than 0.1 mg/dm^3. According to the experimental data that we have built, an adsorption isotherm of petroleum products from the water using the "Sorbent-5" was made and shown in Fig. 4.

As a result, when comparing volumetric (Sorbent-3) and superficial (Sorbent-5) hydrophobization, it is possible to draw the following conclusions:

a. Conducting superficial hydrophobization is most economically advantageous, because the consumption of the hydrophobizator is reduced 10 times.
b. Total pore volume of Sorbent-5 is greater than the total pore volume of Sorbent 3 at 45%, while the sorption capacity increases by 25% (Nikolaeva et al. 2012b).

After the use the modified waste sludge as a filtering load, it is proposed not to regenerate, but to use it as an auxiliary fuel. The heat of combustion of the sample Sorbent-1 and Sorbent-5 was 5354.6 kcal/kg and 5411 kcal/kg respectively (Grigor'ev & Zorin 1982).

We investigated the physical and mechanical properties of the local soils with the addition of waste Sorbent-5 and Sorbent-1 (Nikolaeva et al. 2014). The approximate composition of the fortified soil with cement waste sorbents (0.7...1.2)g of petroleum products per 1g of sorbent. The waste sorbent was injected in dosages of 5, 10, 15 and 20% by the weight of the soil.

The modification of fortified ground using the waste sorbent leads to an increase in residual strength after freeze-thaw cycles. However, partially the increase is due to the decrease of crush strength. The smallest drop of the crush strength and a significant increase in the residual strength after freezing-thawing cycles can be traced at introducing additives of waste sorbent to 10%. The introduction of additives of waste sorbent to fortified clay ground increases 1.4 times of the residual strength after 15 cycles of freezing and thawing.

According to the results of research, there is a beneficial effect of introducing a waste sorbent as a modifier in the fortified ground, consisting in growth of frost resistance and tensile strength in bending.

The calculation of the economic and environmental effects has been made (Semenova 1996). The cost price of the sorbent is 423 USD/t. To calculate the cost of wastewater purification from the petroleum products used, operational data (Kazan's TPP-1) are used. Cost of purification using as sorptive loading of birch activated carbon BAC-0.51 USD/m^3 , using Sorbent-5 will be 0.4 USD/m^3 (assuming sorbent production in situ). There are calculations on the size of prevented ecological damage to water reservoir (technique of definition of prevented ecological damage 1990) that is used for discharge of treated wastewater, which amounted to 21900 USD on a notional tonne reduced mass of pollutants.

CONCLUSION

As a result of the experimental work, sorbent for purification of wastewaters from petroleum waste of thermal power plants is designed. Carbonate sludge can be reused in a cycle of thermal power station. Savings for the purchase of expensive sorption materials are produced.

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