Adsorption Purification of Phenol-Containing Wastewater from Oil Refineries

L A Nikolaeva¹ and N E Aikenova¹²

¹ Department of Water and Fuel Technology, Kazan State Power Engineering University, Krasnoselskaya St., 51, Kazan, 420066, Russia
²Department of Chemistry and Chemical Technology, Aktobe Regional University named after K.Zhubanov, A.Moldagulova Av., 34, Aktobe, 030000, Kazakhstan

E-mail: larisanik16@mail

Abstract. In this paper, the possibility of adsorptive purification of industrial wastewater from oil refineries from phenols by industrial wastes is considered. It is proposed to use carbonate sludge for water treatment of natural water as one of the most accessible materials, which is a large-tonnage waste of energy, for sewage treatment. Phenols in wastewater are hazardous toxic substances. In legal order, sanitary and hygienic standards establish the maximum permissible concentration (MPC) of phenol in water, which is 0.001 mg / dm³. Industrial wastewater containing phenols has a number of difficulties faced by technologists when selecting a technological scheme for cleaning these pollutants, or their disposal. The adsorption isotherm, the kinetic curve of phenol adsorption, the output curve of phenol adsorption under dynamic conditions were constructed, the dynamic sorption capacity of the “GrSM” sorption material was determined, which prove the effectiveness of using carbonate sludge as an adsorbent. A flowchart for the purification of wastewater from phenols is proposed, the calculation of the adsorption filter with the loading of carbonate sludge in the scheme for the purification of wastewater from phenols is performed.

1. Introduction

Enterprises of the petrochemical and refining industries are large consumers of natural water. Water is used for technological operations, the preparation of solutions necessary for the production of products, heating and cooling, washing process equipment. The waste waters of these enterprises contain a wide range of organic substances dissolved in water, including petroleum products and phenols. In the absence of wastewater treatment plants, the anthropogenic pressure on the environment increases, due to the nature of the industrial activity of the enterprise [1-3].

Traditionally used technological schemes of wastewater treatment are obsolete and physically obsolete by now and do not provide high requirements for water quality, therefore, the improvement of wastewater purification technologies from phenol using effective integrated solutions to achieve normal requirements for the quality of treated water with all the associated Phenol contamination is relevant and has a scientific and practical value [4].

The article proposes an adsorption technology for purification of waste oil-containing waters of «Aktobe Oil Refining» LLP with a large-tonnage waste of energy - sludge from chemical water treatment generated during liming and coagulation at the stage of preliminary purification of raw water.
2. Materials and Methods
For the purification of wastewater from phenols with a sorption material developed on the basis of chemical water treatment sludge, an adsorption isotherm and adsorption kinetics are constructed, a purification process flow diagram is considered, and an adsorption filter is calculated. The technical characteristics and adsorption capacity of the material for phenol have been determined.

The work uses chemical water treatment sludge (ChWP) - waste that is generated at the water treatment plant of thermal power plants at the stage of preliminary water purification. In experimental studies, we used dried fine powder sludge [5].

To determine the sorption capacity of granules of the GRSM-1 material, the adsorption isotherm with respect to phenol was obtained, the kinetics of the adsorption process, the adsorption of phenol GRSM-1 was studied under dynamic conditions.

For the purification of wastewater of LLP "Aktobe Oil Refining" from oil products and phenols with a capacity of 60 m$^3$/h, a basic technological scheme is proposed.

In this technological scheme, it is proposed to load the developed hydrophobic GRSM-1 into the adsorption column. The calculation of the adsorption filter FSU 3.0–0.6 with the loading of the developed GRSM-1 was performed.

3. Result and Discussion
Sludge ChWP - waste, which is formed at the water treatment plant of thermal power plants. Experimental studies were conducted with carbonate slurry of Aktobe TPP-1 (humidity-3%). The dried sludge is a fine powder from light yellow to brown color. During the study, a fraction with a particle size of 0.09-0.05 mm was used. X-ray qualitative and phase analysis of sludge on a Bruker P8 ADVANCE diffractometer showed the following chemical composition: calcium CaCO$_3$-73%, brucite Mg(OH)$_2$ - 8%, Portland Ca(OH)$_2$ - 1%, quartz SiO$_2$ - 0.4%, and other substances - 17.6%.

In [6], carbonate sludge is considered as a sorption material for wastewater treatment of industrial enterprises from ITM.

The article discusses the fundamental possibility of purifying wastewater from phenols by sorption material developed on the basis of a ChWP sludge. In earlier works [7], the technical characteristics and the adsorption capacity of the material were determined for emulsified and dissolved petroleum products of the oil from the Shiya field.

he moisture capacity of the ChWP sludge is ~57%, which confirms its high hydrophilicity and poor wettability by non-polar compounds. Therefore, to increase the adsorption capacity and wettability by non-polar compounds, a hydrophobic granular sorption material has been developed and studied on the basis of fine sludge.

The “Silor” liquid was chosen as a hydrophobic agent - a product of chemical decomposition of organosiliconvulcanizates in tetraethyoxylan in the presence of an alkali solution, which in its chemical composition is similar to organosilicon hydrophobic liquids.

Liquid sodium glass was used as a binder. After heat treatment, granules with a particle diameter of 0.5-2.5 mm are formed by rolling. To select the optimal conditions for the manufacture of material granules, studies have been carried out of the dependence of the total pore volume and specific surface area on the processing temperature of the sludge granules. The maximum value of the total pore volume and specific surface is achieved at a temperature of - 700°C. Determination of the specific surface of the material granules was carried out using a "Sorbi-M" by comparing the volumes of gas - nitrogen (adsorbate) sorbet by the granules with a standard sorbent - silica gel.

Thus, a granulated hydrophobic sorption material was obtained: heat-treated at 700°C for 60 minutes, granules with a diameter of 0.5 to 2.5 mm, at a ratio of 1: 2 with a binder with liquid sodium glass, impregnated with 5% - Sylor water emulsion, dried to constant weight. The technological characteristics of the obtained granules of the material were determined (Table 1).
Table 1. Technological characteristics of "GrSM-1".

| Characteristic                   | Value   |
|----------------------------------|---------|
| Particle size, mm                | 0.5-2.5 |
| Bulk density, $\rho_{\text{m}}$, kg/m$^3$ | 670     |
| Humidity, %                      | 2.5     |
| Specific surface, m$^2$/g         | 64.9    |
| Total pore volume, cm$^3$/g       | 0.84    |
| Water absorption, %               | 1.2     |
| Adsorption capacity for iodine, % | 7       |
| Methylene blue adsorption capacity, % | 20     |

To determine the sorption capacity of material granules, an adsorption isotherm with respect to phenol was constructed. The adsorption isotherm is of type V according to the classification of Brunauer, Deming, Deming and Teller (BDDT), a similar S-type isotherm is usually found in the presence of micro and mesopores, and is described by the Freundlich equation: $A = 0.28C^{0.75}$.

![Figure 1](image1.png)

**Figure 1.** Isotherm of phenol adsorption of the GrSM-1 (a) and its appearance in logarithmic coordinates (b).

To determine the time to reach the adsorption equilibrium, the kinetics of the process of phenol adsorption by material granules from model solutions with a certain concentration was studied ($C_{\text{init}} = 100$ mg/dm$^3$) [8-10]. The contact time of the granules with a model solution of 0.33; 0.66; 1; 2; 4; 5; 7 o'clock. It is established that the adsorption equilibrium occurs after 3 hours of contact of the adsorbent with the adsorbate.

For production processes, the adsorption of organic impurities in dynamic conditions is of the greatest importance. The process of phenol adsorption was investigated using granulated GrSM-1 (fractions 0.5-2.5 mm) in a laboratory setup, which is a filter column 2.5 cm in diameter. The concentration of phenol in the model solution is 1.5 mg/dm$^3$, is medium at the entrance to the adsorption filter in the wastewater treatment system. The height of the loading layer is - 20 cm, weight - 54.38 g, filtration speed - 3.5 m/h. The breakthrough is fixed at a concentration of 0.001 mg / dm$^3$. Figure 3 shows the output curve of phenol adsorption under dynamic conditions. During the experiment, the dynamic sorption capacity (DSC), the total sorption capacity (TSC) "GrSM-1" was determined. The result is presented in table 2.
According to the Shilov equation, the time $\tau$ and the coefficient $K$ of the protective action of the GrSM-1 layer are calculated: $\tau = 95.2$ h; $K = 612.6$ h/m.

For the calculation of technical and economic indicators, the use of a sorbent, GrSM-1 in the wastewater treatment system of “Aktobe Oil Refining” LLP is proposed.

The greatest consumption of water in industrial installations is noted at the stage of oil preparation, in the process of its dehydration and desalting. Oil is pumped into the pump room and comes in the form of a mixture together with the washing water into the electrohydrators, where desalination and dehydration by the action of electric current takes place. The water separated on the installations of electrical desalting plant is discharged into a special sewage network.
During primary oil refining in atmospheric vacuum tubulars (AVT) to obtain light distillates and oil fractions. Oil after electrical desalting plant passes heat exchangers, where it contacts with water - it cools, condenses in heat exchangers and condensers.

Vacuum in barometric condensers for mixing AVT vacuum columns is created due to the direct contact of water with oil product vapors and gases. As a result, the waste water is polluted with vapors of petroleum products and hydrogen sulfide.

Due to the aggressiveness of sulfur compounds to the metal processing equipment, their presence in commercial petroleum products is not allowed. Oil products are purified from sulfur compounds by washing with an aqueous solution of alkali (caustic soda). In this case, hydrogen sulfide, mercaptans and other sulfur compounds, as well as phenols, are transferred from petroleum products to alkaline solution. After repeated use of alkaline solution containing a large amount of sulfur compounds, as well as other pollutants, is discharged into a special sewer network.

At refineries, industrial storm sewage is generated, which is discharged into the sewage system and then fed to wastewater treatment plants. Sources of pollution include process wastewater from condensation equipment, as well as the recovery tanks of the MEA solution. Table 3 shows the chemical composition of the description of the wastewater of “Aktobe Oil Refining” LLP.

| The name of indicators | Unit of measurement | Concentration | MPC       |
|------------------------|---------------------|---------------|-----------|
| Hydrogen ions          | pH units            | 7.34          | 6.5-8.5   |
| Dry residue            | mg/dm³              | 2310          | -         |
| Total hardness         | mg-eq/dm³           | 4.6           | -         |
| Oil products           | mg/dm³              | 96.8          | 0.1-5     |
| SAS                    | mg/dm³              | 0.490         | 0.5       |
| Phenols                | mg/dm³              | 0.1           | 0.001     |
| Ammonia nitrogen       | mg/dm³              | 5.53          | -         |
| Common iron            | mg/dm³              | 2.92          | 2-20      |
| Cadmium                | mg/dm³              | 0.0001        | 0.01-0.6  |
| Manganese              | mg/dm³              | 0.254         | -         |

For wastewater treatment of “Aktobe Oil Refining” LLP from petroleum products and phenols with a capacity of 60 m³/h, the following flow chart [11] is presented in Figure 4.

In the shop for processing by-products and wastes, wastewater is formed during the decomposition of sodium phenolate with sulfuric acid. Wastewater contains mostly phenol and acetone. Together with the wastewater from the decomposition shop of isopropyl benzene hydroperoxide, containing up to 30 g/l of phenol, they fall into local cleaning, which consists in the extraction of phenol with diisopropyl ether or acetophenone. Pre-waste water is acidified with sulfuric acid in tank 3 to pH = 1. From here, they are sent through an average 4 for irrigation into column 6 for adsorption of volatile substances from the gases. Extraction of phenol is carried out in pulsation columns 7 with intermittent flow of the extractant (75 pulsations per 1 minute). The ratio of ether and wastewater is 1:3, the degree of extraction of phenol in wastewater when using diisopropyl ether is 99.3%, while using acetophenone is 99.6%.

The extract saturated with phenol is fed to the rectification for the regeneration of the extractant. Rectification is carried out in a packed column 8 with a reflux number of 0.5-1 to a residual content of phenol in the extractant 7-1 mg/l. Pairs of ether from the column (at a temperature of 68-69°C) enter the reflux condenser 9 and the condenser 10; the condensed ether is collected in tank 14 and returned to extraction. The consumption of fresh air to compensate for losses in one cycle is 1% of its quantity circulating in the system. The regenerated phenol enters the tank 15 and returns to production. Water
is subjected to Stripping from the ether in column 12 and after cooling in the refrigerator 13 is discharged into the sewer.

Figure 4. Schematic diagram of the dephenolation of wastewater “Aktobe Oil Refining” LLP. 1 – collective wastewater tank; 2 – pressure tank; 3 – tank for acidification of wastewater; 4 – averaging tank; 5 – pumps; 6 – adsorption column; 7-I and 7-II - extraction columns; 8 - distillation columns; 9 – reflux condenser; 10 – capacitor; 11 – boiler; 12 – Stripping column; 13 – fridge; 14 – capacity for ether; 15 – capacity for phenol; I – phenolic wastewater; II – sulfuric acid; III – exhaust gases; IV – extractant (ether); V – extract; VI – extractant (ether) vapors; VII – cooling water; VIII – cooling brine; IX – pairs; X – phenol; XI – drain to sewer.

In this technological scheme, it is proposed to load the developed hydrophobic granulated material “GrSM-1” into the adsorption column 6. The calculation of this adsorption filter FSU 3.0–0.6 with the loading of the developed sorption material “GrSM-1” was made. Table 4 presents the initial data for the calculation.

Table 4. Original data for the calculation of the adsorption filter with loading "GrSM-1".

| Parameter                                              | Value         |
|--------------------------------------------------------|---------------|
| Specific free volume (porosity), ε                      | 0.407         |
| The density of wastewater ρ_w.w, kg/m^3                 | 1000          |
| The coefficient taking into account the shape of particles, F | 0.9           |
| Loading height H, m                                      | 2.5           |
| Kinematic viscosity coefficient of water (at 20 °C), μ     | 1.004·10^{-3} |
| Number of filters, n                                     | 1             |
| Filter performance Q_p, m³/h (m³/s)                     | 25 (0.0069)   |
| Filter area S_{adv}, m²                                  | 7.1           |
| Bulk density ρ_b, kg/m³                                  | 670           |
| Filtering speed, m/h                                     | 3.5           |
Fictitious flow rate $\omega_{\text{fic}}$, m/s, is calculated by the formula

$$\omega_{\text{fic}} = \frac{Q_{\text{per}}}{S_{\text{ads}}} = \frac{0.069}{7.1} = 0.0097 \text{ m/s}$$  \hspace{1cm} (1)

The true flow rate $\omega_{\text{tr}}$, m/s, is calculated by the formula

$$\omega_{\text{tr}} = \frac{\omega_{\text{fic}}}{\varepsilon} = \frac{0.0097}{0.407} = 0.024 \text{ m/s}$$  \hspace{1cm} (2)

The apparent density of the adsorbent $\rho_{\text{app local}}$, kg/m$^3$, is calculated by the formula

$$\rho_{\text{app}} = \frac{\rho_{\text{sol}}}{1 - \varepsilon} = \frac{560}{1 - 0.407} = 944.35 \text{ kg/m}^3$$  \hspace{1cm} (3)

The particle size of the adsorbent: $d_p = 0.002$ m.

The specific surface $a_v$, m$^2$/m$^3$, is calculated by the formula

$$a_v = \frac{6(1 - \varepsilon)}{d_p} = \frac{6(1 - 0.407)}{0.002} = 1779 \text{ m}^2/\text{m}^3$$  \hspace{1cm} (4)

Determine the flow of flow in the layer.

Reynolds number is calculated by the formula

$$Re = \frac{\omega_{\text{tr}} d_p \rho_{\text{w}} \cdot \omega_{\text{tr}}}{\mu} = \frac{0.0024 \cdot 0.002 \cdot 1000}{1.004 \cdot 10^{-3}} = 4.78$$  \hspace{1cm} (5)

The coefficient of friction is found depending on the nature of the movement [12]:

1) $Re < 50 \lambda = \frac{220}{Re}$;

2) $Re = 50 - 7200 \lambda = \frac{11.6}{Re^{0.25}}$;

3) $Re > 7200 \lambda = 1.26$

The coefficient in this case is equal to $\lambda = \frac{220}{4.78} = 46.025$

The pressure drop of the bulk layer $\Delta P$, Pa, is determined by the formula

$$\Delta P = \lambda \cdot \frac{H}{d_p^2} \cdot \rho_{\text{w}} \cdot \omega_{\text{tr}}^2 = 46.025 \cdot 2.5 \cdot \frac{1000 \cdot 0.0024^2}{2} = 331.8 \text{ Pa}$$  \hspace{1cm} (6)

The mass of GrSM-1 for loading one adsorption filter $m_c$, kg, is calculated by the formula

$$m_c = \rho_b \cdot S_{\text{ads}} \cdot H = 670 \cdot 7.1 \cdot 2.5 = 11892 \text{ kg}$$  \hspace{1cm} (7)
The penetration of the adsorbate into the adsorbent grain is a diffusion process and, therefore, is characterized by a diffusion coefficient. The diffusion coefficient \( D \) is the amount of a substance diffusing into a unit of time through a square centimeter of surface with a concentration gradient equal to one \([13]\).

The exact determination of the diffusion coefficient is made by complex formulas. In technical adsorption, it should be limited to its definition \( D \), m\(^2\)/s, according to the approximate dependence \([6]\)

\[
D = \frac{K \cdot r^2}{\pi^2 \cdot \tau_{0.5}}, \quad (8)
\]

where:

- \( r \) – is the radius of the granules;
- \( K \) – coefficient depending on the shape of the granules;
- \( \tau_{0.5} \) – is the half-time of the adsorption capacity, i.e. period of time elapsed from the beginning of the experiment to the moment when the amount of the adsorbed substance reaches 50% of the equilibrium adsorption capacity \([13]\).

For particles of a spherical shape, the coefficient \( K \) is equal to 0.308.

Time \( \tau_{0.5} = 120 \) s (the half-time of the sorption tank “GrSM-1” for the averaged oil product is gasoline, oil).

The diffusion coefficient of phenol molecules inside the adsorbent grain is determined by the equation

\[
D = \frac{K \cdot r_p^2}{\pi^2 \cdot \tau_{0.5}} = \frac{0.308 \cdot 0.001^2}{3.14^2 \cdot 120} = 5.201 \cdot 10^{-10} \text{m}^2/\text{s}
\]

The kinematic viscosity coefficient \( \nu \), m\(^2\)/s, is determined by the formula

\[
\nu = \frac{\mu}{\rho_{ww}} = \frac{1.004 \cdot 10^{-3}}{1000} = 1.004 \cdot 10^{-6} \text{m}^2/\text{s} \quad (9)
\]

To determine the mass transfer coefficient, it is necessary to determine the Prandtl diffusion criterion \([14-15]\) using the formula

\[
Pr_{\text{diff}} = \frac{\nu}{D} = \frac{1.004 \cdot 10^{-6}}{5.201 \cdot 10^{-10}} = 1930 \quad (10)
\]

The reduced diameter \( d_{\text{red}} \), m, is calculated by the formula \( d_{\text{red}} \)

\[
d_{\text{red}} = \sqrt[3]{6 \left(\frac{\pi \cdot d^2}{4}\right) \cdot l_i} = \sqrt[3]{6 \left(\frac{3.14 \cdot 0.002^2}{4}\right) 0.002} = 0.0023 \text{ m} \quad (11)
\]

\[
L = \frac{\pi \cdot d_{\text{red}}}{2} = \frac{3.14 \cdot 0.0023}{2} = 0.0036 \text{ m} \quad (12)
\]

The mass transfer coefficient \( \beta \), m/s, is calculated by the formula

\[
\beta = 0.62 \left(\frac{\Delta P \cdot e \cdot v}{\alpha \cdot H \cdot L \cdot \rho_{ww}}\right)^{\frac{1}{3}} \cdot 1930^{\left(\frac{2}{3}\right)} = 0.62 \left(\frac{331.38 \cdot 0.407 \cdot 1.004 \cdot 10^{-6}}{1779 \cdot 2.5 \cdot 0.0036 \cdot 1000}\right)^{\frac{1}{3}} \cdot 1930^{\left(\frac{2}{3}\right)} \quad (13)
\]

\[
= 7.3 \cdot 10^{-6} \text{ m/s}
\]
The volume coefficient of mass transfer $\beta_y$, s$^{-1}$, is calculated by the formula

$$\beta_y = \beta \cdot a_v = 7.9 \cdot 10^{-6} \cdot 1779 = 0.014 \text{ s}^{-1}$$

(14)

4. Conclusion
In this work, the sorption capacity of granules of the material is determined, the adsorption isotherm with respect to phenol is constructed, and the adsorption curve for the study of phenol adsorption kinetic processes is constructed, and the adsorption curve of phenol GrSM-1 is constructed under dynamic conditions. Also carried out experimental studies on the adsorption purification of phenol-containing wastewater of “Aktobe Oil Refining” LLP using granulated modified carbonate sludge (GrSM-1). Purification efficiency $E> 90\%$. The calculation of the adsorption filter with the loading of the lubricant in the scheme of purification of wastewater from phenols was made.

5. Acknowledgments
The work was performed in the framework of the basic part of the state task in the field of scientific activity (No. 13.6384.2017 / BP).

References
[1] Sun X, Wang C, Li Y, Wang W and We J 2015 Treatment of phenolic wastewater by combined UF and NF/RO processes Desalination 355 68-74
[2] Lakshmi S, Harshitha M, Vaishali G, Keerthana S and Rhea M 2016 Studies on different methods for removal of phenol in waste water- Review Int. J. of Science, Eng. and Technology Research 5(7) 2488-96
[3] Cordova Villegas L G, Mashhadi N, Chen M, Mukherjee D, Taylor K E and Biswas N 2016 A Short Review of Techniques for Phenol Removal from Wastewater Current Pollution Reports 2 157-67
[4] Franz M, Arafat H A and Pirto N G 2000 Effect of chemical surface heterogeneity on the adsorption mechanism of dissolved aromatics on activated carbon Carbon 38(13)
[5] Nikolaeva L A 2016 Adsorbciyonsnaya ochistka stochny`h vod modificzirovannym karbonatnym shlamom [Adsorption treatment of industrial wastewater with modified carbonate sludge: DSc thesis ] (Kazan: KGEU)
[6] Sklavos S, Gattidou G, Stasinakis A S and Haralambopoulos D 2015 Use of solar distillation for olive mill wastewater drying and recovery of polyphenolic compounds J. Environ. Manag. 162 46-52
[7] Tran V S, Ngo H H, GuoW, Zhang J, Liang S, Ton-That C and Zhang X 2015 Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water Bioresource Technology 182 353-63
[8] Kulkarni S J and Kaware J P 2013 Review on Research for Removal of Phenol from Wastewater IJSRP 3(4) 161089
[9] Mukherjee S, Basak B, Bhunia B, Dey A and Mondal B 2013 Potential use of polyphenol oxidases (PO) in the bioremediation of phenolic contaminants containing industrial wastewater Environ. Sci. Biotechnol. 12 61-73
[10] Masomi M and Ghoreyshi A A 2014 Adsorption of Phenolic Compounds onto the Activated Carbon Synthesized from Pulp and Paper Mill Sludge: Equilibrium Isotherm, Kinetics, Thermodynamics and Mechanism Studies Int. J. Eng. 27(10) 1485-94
[11] Mukherjee R and De S 2014 Adsorptive removal of phenolic compounds using cellulose acetate phthalate–alumina nanoparticle mixed matrix membrane J. Hazard. Materials 265 8-19
[12] Mohammadi S, Kargari A, Sanaeepour H, Abbassian K, Najafi A and Mofarrah E 2015 Phenol removal from industrial wastewaters: a short review Desalination and Water Treatment 53(8) 2215-34

[13] Sciban M, Klasnja M and Skrbic B 2006 Modified Hardwood Sawdust as Adsorbent of Heavy Metal Ions from Water Wood Science and Technology 40(3) 217-27

[14] Carvajal-Bernal A M, Gómez F, Giraldo L and Moreno Pirajá JC 2015 Chemical modification of activated carbons and its effect on the adsorption of phenolic compounds Ingeniería Y Competitividad 17(1) 109-19

[15] Zwain H M, Vakili M and Dahlan I 2014 Waste Material Adsorbents for Zinc Removal from Wastewater: A Comprehensive Review Int. J. of Chemical Eng. 2014 347912