

## Wastewater Treatment of Industrial Enterprises from Phenols with Modified Carbonate Sludge

Aikenova, Nuriya

Department of Chemistry and Chemical Technology, K. Zhubanov Aktobe Regional University

Sarsembin, Umbetaly

Department of Ecology, K. Zhubanov Aktobe Regional University

Almuratova, Karlyga

Department of Chemistry and Chemical Technology, K. Zhubanov Aktobe Regional University

<https://doi.org/10.5109/7160900>

---

出版情報 : Evergreen. 10 (4), pp.2244-2254, 2023-12. 九州大学グリーンテクノロジー研究教育センター

バージョン :

権利関係 : Creative Commons Attribution 4.0 International

# Wastewater Treatment of Industrial Enterprises from Phenols with Modified Carbonate Sludge

Nuriya Aikenova<sup>1,\*</sup>, Umbetaly Sarsembin<sup>2</sup>, Karlyga Almuratova<sup>1</sup>

<sup>1</sup>Department of Chemistry and Chemical Technology, K. Zhubanov Aktobe Regional University, Republic of Kazakhstan

<sup>2</sup>Department of Ecology, K. Zhubanov Aktobe Regional University, Republic of Kazakhstan

\*Author to whom correspondence should be addressed:

E-mail: nuriyaikenova@yahoo.com

(Received August 4, 2023; Revised November 13, 2023; accepted December 9, 2023).

**Abstract:** Today, the topic of the global problem of providing the population with water suitable for consumption is investigated regularly, and every year the urbanisation of cities and, consequently, industrialization grows, and when water is used for technical needs, it must be treated to the normative maximum permissible concentrations, which is an energy- and resource-intensive process. To effectively treat wastewater from various pollutants, industrial wastes are increasingly being used, which show high efficiency of wastewater treatment and are inexpensive. It is the study of the specifics and peculiarities of the use of production wastes that is the purpose of this study. During the research, methods such as analysis and experimentation were used. The article proposes to use carbonate sludge as an adsorbent – a large-tonnage waste from chemical water treatment plants at thermal power plants. The study is devoted to the presentation and analysis of the results obtained in the development of a sorption material known as granular modified carbonate sludge (GMCS). To evaluate the interaction of carbonate sludge with phenol, an adsorption isotherm was constructed. In addition to the isotherm, the study also included the construction of an adsorption output curve under dynamic conditions. Based on the data, the environmental efficiency of wastewater treatment from phenols was calculated. This calculation considered the initial concentration of phenol in the wastewater, the amount of phenol adsorbed by GMCS, and the resulting decrease in the concentration of phenol after treatment. The environmental impact of using GMCS for phenol removal was determined by quantifying eco-efficiency. The practical significance of this research is that it can help to reduce the pollution of water systems, improve sanitary conditions, and protect human health and ecosystems.

Keywords: adsorption, granular modified carbonate sludge, coagulation, colloidal impurities, solution

## 1. Introduction

Industrial growth driven by technological advancements has led to increased environmental pollution. The Aktobe region in Kazakhstan is a major industrial area consuming large amounts of natural water. Wastewater discharged from industrial enterprises in the region contains high concentrations of pollutants, surpassing the maximum allowable levels for fisheries, household, and cultural water use. Inadequate treatment of wastewater by these enterprises contributes to the environmental impact. The analysis of wastewater in the region, particularly from oil production, petrochemical, and oil-refining industries, reveals high levels of organic pollutants.

Humanity is facing severe environmental problems

caused by industrial wastewater emissions, driven by population growth, intensive agriculture, and rapid industrialization. The lack of wastewater treatment technology and the discharge of wastewater below safe environmental levels worsen the water crisis in developing countries.

Water purification research focuses on effective methods to remove pollutants, including emerging pollutants known as nanoporous carbons (NPCs). NPCs, which include pharmaceuticals, hormones, pesticides, and other compounds, pose challenges to existing water treatment systems, and can harm human health and the environment. Their impact on ecosystems must be controlled to prevent detrimental effects. NPCs have gained attention in the 21st century as hazardous water pollutants, despite being discovered in the 19th century. Their extensive use in various sectors of the economy

contributes to their significant environmental impact.<sup>1),2)</sup>

Some scholars have already conducted studies on similar topics. Among them, several works are worth mentioning. E. O. Ezugbe and S. Rathilal<sup>3)</sup> studied membrane technologies in wastewater treatment as a modern method of water purification. The features of membrane modules, their contamination and purification were also identified and considered. S. Singh et al.<sup>4)</sup> was able to investigate the possibility of using SSBC as a safe and productive wastewater treatment method. The use of SSBC helps to purify water from heavy metals, antibiotics, phenolic compounds and more. Scientists I. Radelyuk et al.<sup>5)</sup> studied the specifics of cleaning operations at oil refineries in Kazakhstan. The results showed that the wastewater of enterprises had many pollutants that complicated the process of water treatment and did not meet the standards of the World Health Organization (WHO). The studies are of great importance in the field of wastewater treatment of industrial enterprises. However, none of them highlighted the features of water purification from phenol. It was this that indicated the need for a specific study.

This research is important because it addresses a pressing environmental issue in an industrial region, offers potential solutions to emerging pollutants, and contributes to global efforts to improve wastewater treatment methods, particularly for the removal of phenolic compounds. The study aims to provide valuable insights into the use of carbonate sludge as an adsorbent, which could have far-reaching implications for environmental protection and sustainable industrial practices.

The scientific novelty of this work lies in its exploration of the novel application of adsorbent carbonate sludge, a large-tonnage waste product from chemical water treatment plants at thermal power plants, for the efficient removal of phenols from industrial wastewater. This approach offers a unique and potentially groundbreaking solution to a specific and pressing environmental problem in the Aktobe region of Kazakhstan, addressing the presence of emerging pollutants.

The practical significance of this research is to improve the environmental sustainability of industrial enterprises by providing an effective method for wastewater treatment, which can help these industries meet environmental standards and reduce their negative impact on local ecosystems. In addition, it has broader implications for water treatment practices globally, as the innovative use of carbonate sludge as an adsorbent material has the potential to be applied in various industrial contexts, offering a sustainable and cost-effective solution for removing phenolic compounds and other emerging pollutants from wastewater, thereby enhancing water quality and safeguarding public health.

## 2. Materials and methods

A potential solution for industrial wastewater treatment involves the utilisation of granular modified carbonate sludge (GMCS) as an adsorbent. GMCS is obtained through a heat treatment process at 600°C for 60 minutes. The resulting granules have a diameter ranging from 0.5 to 2.5 mm. To enhance their stability, a liquid sodium binder is used at a ratio of 1:2, along with impregnation of a 5% Silor water emulsion into the granules made of glass.

When determining the concentration of phenols, the concept was used as a “phenol index” – the mass concentration in water of compounds of the phenol group (phenol, cresol, hydroquinone, resorcinol, etc.). A model phenol solution with a concentration of 100 mg/dm<sup>3</sup> is prepared by dissolving a sample of phenol (analytical grade according to TU 6-09-40-3245-90) in distilled water, in one stage, because phenol is highly soluble in water, resulting in a true solution.

The method of gas-liquid chromatography was used for analysis to determine the concentration of phenol. This analytical method is based on the use of several stages of reactions for the isolation of phenols with subsequent determination of its concentration. In the first stage, phenol is brominated in an environment with a low acid content, and the bromine reduction reaction is carried out. Bromine that has not reacted with sodium sulphate is restored. To isolate bromine compounds, an extraction reaction of tribromophenol with a solution of hexane should be carried out. During extraction, phenol is released, its concentration is examined by gas-liquid chromatography. The mass concentration of phenol is calculated by the following formula (1):

$$X \frac{S_x}{k}, \quad (1)$$

where X – the mass concentration of phenol, µg/dm<sup>3</sup>; S<sub>x</sub> – the area of the peak on the chromatogram, mm<sup>2</sup> or units. accounts; k – the coefficient of the constructed calibration curve.

For industry, an important role is played by the adsorption capacity of the material under dynamic conditions. Under dynamic conditions, the adsorption characteristic of the sorption material was determined by the frontal chromatographic method. This method is described by passing the test water through the column, which contains the sorption material. The method is based on the saturation of the sorption material with contaminants. In this method, water saturated with phenols is passed through the sorption material from the top of the column, then the coefficient of water purification is calculated. The dynamic sorption capacity (DSC) is calculated by the formula, mg/g (2):

$$DSC \frac{V_p C}{m}, \quad (2)$$

where  $V_p$  – the volume of dephenolized solvent,  $\text{dm}^3$ ;  $C$  – equilibrium concentration of the solution,  $\text{mg}/\text{dm}^3$ ;  $m$  – mass of the sorption material, g.

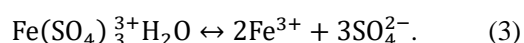
The column has a diameter of 25 mm and a sorption material layer height of 20 mm. The weight of the sorption material is 54.38 g, and the filtration rate is 3.5 m/h. The breakthrough of phenols in water is observed at a concentration of  $0.001 \text{ mg}/\text{dm}^3$ . Adsorption capacity is determined by the “breakthrough” of phenol in the filtrate. The full dynamic adsorption capacity of the sorption material is determined by saturation of the sorption material with phenols, where equal values of phenol concentration are observed in the initial sample and in the filtrate.

### 3. Results

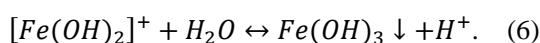
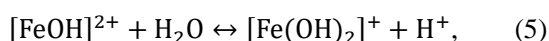
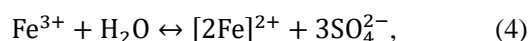
#### 3.1. Use of lime milk in water treatment.

Milk of lime ( $\text{Ca}(\text{OH})_2$ ) is commonly used in water treatment to soften water. It reduces water hardness by forming soluble carbonates through a reaction with calcium and magnesium bicarbonates. Softening water is crucial due to the presence of high mineral content, such as calcium and magnesium, in hard water. Hard water can lead to issues like scaling, reduced lathering of soap, and reduced efficiency of water-related appliances. Milk of lime, a suspension of calcium hydroxide in water, is added to the water, dissolving the calcium hydroxide, and producing calcium and hydroxide ions. The hydroxide ions then react with bicarbonate ions from calcium bicarbonate and magnesium bicarbonate, creating insoluble carbonates.<sup>6)</sup>  $\text{Fe}(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$  is used as a coagulant in the coagulation process. It undergoes hydrolysis according to the following scheme:

1. Dissociation of coagulant molecules (3):



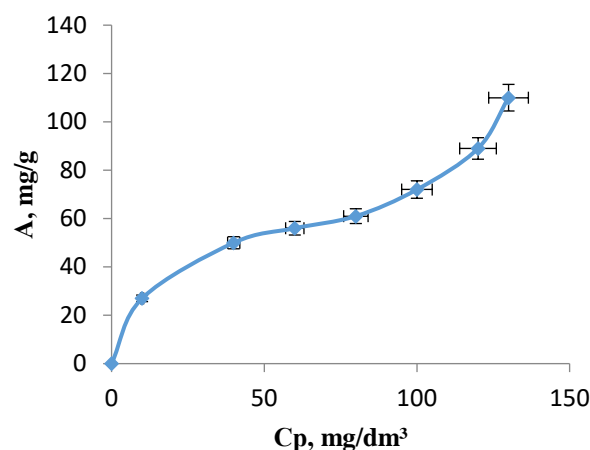
2. Three step hydrolysis (4-6):



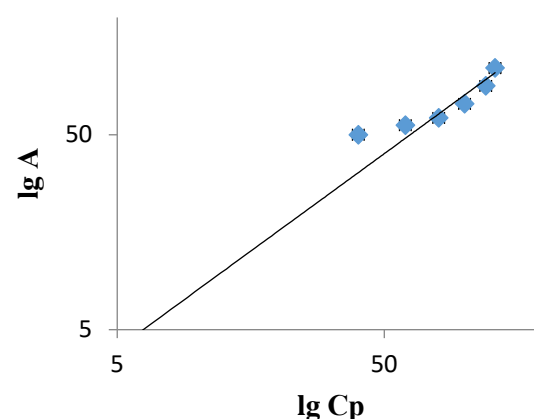
Iron hydroxide ( $\text{Fe}(\text{II})$ ) is oxidised to form poorly soluble iron hydroxide ( $\text{Fe}(\text{III})$ ) during coagulation.  $\text{Fe}(\text{III})$  particles connect to form chains, where colloidal impurities in water are adsorbed. The chains create pores filled with water, forming flakes that settle with suspended particles due to gravity. This process forms carbonate sludge in chemical water treatment.

To analyse the composition of the carbonate sludge, X-ray qualitative-phase analysis is conducted using a D8 ADVANCE diffractometer from Bruker. The composition includes Calcite  $\text{CaCO}_3$  (75%), Brucite  $\text{Mg}(\text{OH})_2$  (4%), Portlandite  $\text{Ca}(\text{OH})_2$  (0.5%), Quartz  $\text{SiO}_2$  (0.1%), Limonite  $\text{Fe}(\text{OH})_3$  (6%), and other substances (14.4%). The hydrophilic nature of carbonate sludge is increased by modifying it with Sailor hydrophobizing liquid. This modification enhances its adsorption capacity for organic pollutants, particularly phenol.

To evaluate the adsorption properties of carbonate sludge, a curve of adsorption of phenol by powdered modified carbonate sludge (PMCS) was constructed. The experiment on the study of the process of adsorption of phenol PRMS is carried out in a static mode. Isotherms are shown in Figure 1.



a)



b)

**Fig. 1:** Phenol adsorption isotherm of PMCS (a) and its form in logarithmic coordinates (b)<sup>7)</sup>.

The adsorption isotherm is classified as type IV according to BDDT. This type is characterized by the

presence of micro- and mesopores and shows an S-shaped curve. The adsorption behaviour can be described using the Freundlich equation:  $A = 0.28 C^{0.75}$ .<sup>8)</sup>

When processing the statistical data of the phenol adsorption isotherm of SCMS by a graphical method, its compliance with the Langmuir KL, BET (Brown, Emmett,

Teller) KBET, Freundlich KF, and Redlich-Petterson KR equations for the adsorption coefficient  $a_m$  and the tangent of the angle  $\alpha$  and  $\beta$  was verified.<sup>9)</sup> The model's efficiency is evaluated using the correlation coefficient  $R^2$ . The processing outcomes are displayed in Table 1.

Table 1. Results of calculating phenol adsorption isotherms by a graphical method.

Model parameters												
Langmuir model			BET model			Freundlich model			Redlich-Petterson model			
$K_L$	$a_m$	$R^2$	$K_{БЭТ}$	$a_m$	$R^2$	$K_L$	$a_m$	$R^2$	$K_R$	$\alpha$	$\beta$	$R^2$
0.005	146.9	0.965	0.001	10.1	0.9	0.02	1.4	0.99	9.2	0.453	0.983	0.921

Source: compiled by the authors.

The adsorption of phenol by presumably renewable material sorbent (PRMS) was best described using the Freundlich model, as indicated by the calculated data. The correlation coefficient  $R^2$  can be used to assess the efficiency of the adsorption process.<sup>10)</sup> The Freundlich model is commonly used to characterise adsorption phenomena, especially when ideal conditions are not met. It is an empirical equation that relates the concentration of the adsorbate (phenol) to the amount adsorbed onto the adsorbent.

Dynamic adsorption of organic pollutants is crucial for industrial processes. In a study on phenol adsorption, a hydrophobic sorption material called GMCS was used. GMCS was produced by granulating carbonate sludge with liquid sodium glass (LSS) as a binder, and then impregnating the granules with a water-repellent Silor emulsion. The technological properties of the GMCS material granules were determined (Table 2).

Table 2. Technological characteristics of the GMCS.

No.	Characteristic	Meaning
1	Size, mm	0.5-2.5
2	Bulk density, $\rho_n$ , kg/m <sup>3</sup>	670
3	Wetness, %	2.5

4	Specific surface, m <sup>2</sup> /g	76
5	Total pore volume, cm <sup>3</sup> /g	0.84
6	Water absorption, %	1.2
7	Ash content, %	81

Source: compiled by the authors.

An experiment was conducted to study the adsorption rates of GMCS under dynamic conditions. A laboratory adsorption column was used with a model solution containing phenols at a concentration of 5 mg/dm<sup>3</sup>. The aim was to simulate real-world scenarios where the adsorbent is exposed to a continuous flow of solution.

By passing the model solution through the adsorption column, the adsorption efficiency of GMCS was determined. The experiment resulted in an adsorption efficiency of 99%, indicating that 99% of the phenols were successfully adsorbed by GMCS. This high efficiency demonstrates the excellent performance of GMCS in removing phenols from the solution.<sup>11)</sup> To assess the quality of GMCS and prevent potential secondary contamination of the filtrate, distilled water was passed through the sorption material bed. The results of this evaluation can be found in Table 3.

Table 3. Indicators of water quality when passing through the adsorbent GMCS.

Water volume, dm <sup>3</sup>	General hardness, mg-eq/dm <sup>3</sup> (MPC* not standardised)	Total alkalinity, mg-eq/dm <sup>3</sup> (MPC* = 0-400 mg-eq/dm <sup>3</sup> )	Total iron, mg/dm <sup>3</sup> (MPC* = 0.05-0.1 mg/dm <sup>3</sup> )	Silicon content, mg/dm <sup>3</sup> (MPC* = 10 mg/dm <sup>3</sup> )
0.05	4.6	1.8	2.92	11
0.1	4.6	2.11	2.15	10.4
0.4	4.6	3.53	2.05	10.0
0.8	4.6	3.14	1.03	9.4
1.2	4.6	1.16	0.67	8.0
10	4.6	1.21	0.10	6.15

Note: \* harmful substances in the waters of water bodies of fishery importance.

Source: compiled by the authors.

The experiment confirmed that passing distilled water through granular sorption material did not result in secondary contamination from the material's substances. This finding is crucial for preventing environmental damage from water pollution.

The use of granular sorption material effectively captures and removes contaminants from water without introducing additional pollutants. This characteristic is highly desirable in water treatment processes to ensure the treated water remains free from harmful substances. Preventing environmental damage from water pollution requires a comprehensive approach involving financial, technological, and organisational measures. These measures collectively minimise the adverse impact on the aquatic environment and reduce economic costs for enterprises.

Financial measures involve allocating resources to support efficient water treatment systems, mitigating the release of pollutants and preserving the natural ecosystem. Investing in water treatment technologies helps prevent further contamination of water bodies by enterprises. Environmental damage prevented during the treatment of industrial wastewater with GMCS is calculated based on pollutant mass indicators and coefficients considering harmful environmental factors. The environmental efficiency of phenol wastewater treatment technology is presented in Table 4.

Table 4. Calculation of the prevented environmental damage to the environment during the treatment of industrial wastewater GMCS.

No.	Name of cost indicators	Price, thousand USD/year
1	The amount of prevented environmental damage to the reservoir as a result of environmental protection activities	36.4
2	The amount of prevented environmental damage from soil degradation as a result of environmental activities	1.15
Total		37.5

Source: compiled by the authors.

Implementing GMCS wastewater treatment technology has shown a significant reduction in pollutant emissions of 5.2 conventional tons per year. This quantitative reduction highlights the effectiveness of the technology in removing pollutants and preventing their release into the environment.<sup>12)</sup>

Reducing pollutant emissions provides multiple benefits, including protecting water bodies and preserving the aquatic ecosystem. It also contributes to overall environmental preservation and supports sustainable development. In terms of economic impact, the estimated payback period for implementing GMCS is 5 years. This indicates the time required to recover the initial

investment through cost savings or financial benefits.<sup>13)</sup>

Overall, the reduction in pollutant emissions and the 5-year payback period demonstrate the effectiveness of GMCS as a wastewater treatment technology. Implementing this technology and embracing environmental protection measures can lead to significant environmental benefits, regulatory compliance, and potential financial advantages.

### 3.2. Using chemical water treatment sludge in wastewater treatment

The chemical water treatment sludge exhibits a strong affinity for water and does not easily interact with non-polar substances due to its low wettability. It has a moisture capacity of -57%. In order to improve its ability to adsorb non-polar compounds and enhance its wettability, a hydrophobic granular sorption material was developed using this sludge. To achieve this, the sludge was treated with a hydrophobic agent known as "Silor", which shares a similar composition with organosilicon hydrophobic liquids. To bind the granules together, a liquid sodium glass was employed.

To determine the most suitable conditions for manufacturing the material granules, extensive research was conducted to investigate the correlation between processing temperature and total pore volume as well as specific surface area. The highest values for these parameters were obtained when the temperature reached 600°C. Table 5 presents the characteristics of the resulting material granules.

Table 5. Technological features of "GrSM-1"<sup>14)</sup>.

Characteristics	Value
Size, mm	from 0.5 to 2.5 mm
Bulk density, $\rho_m$ , kg/m <sup>3</sup>	670.5309
Wetness, %	2.49
Specific surface, m <sup>2</sup> /g	63.999
Total pore volume, sm <sup>3</sup> /g	0.83941
Water absorption, %	1.2001
Adsorption capacity for iodine, %	7.03
Methylene blue adsorption capacity, %	20.0001

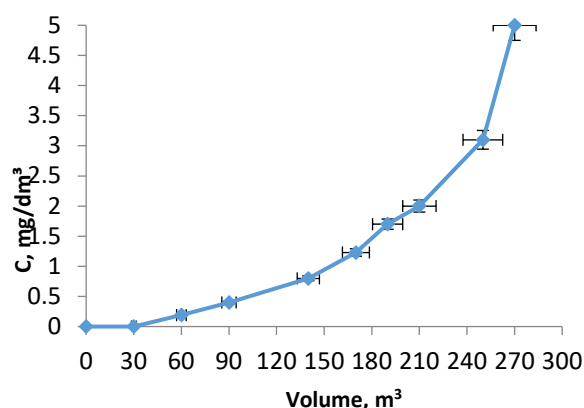
In order to evaluate the sorption capacity of granular material, a dedicated adsorption isotherm was formulated specifically for phenol. The adsorption isotherm demonstrates a type V behaviour as per the Brunauer, Deming, Deming, and Teller (BDDT) classification. Similar S-shaped isotherms are typically observed when micro and mesopores are present. This particular isotherm can be described using the Freundlich equation:  $A = 0.28 C^{0.75}$ .

The kinetics of phenol adsorption by material granules at a specific concentration ( $C_{init} = 100 \text{ mg/dm}^3$ ) were

studied to determine the time required for adsorption equilibrium. The granules were exposed to the model solution for various durations: 0.33, 0.66, 1, 2, 4, 5, and 7 hours. A state of equilibrium was reached following a contact time of 3 hours between the adsorbent and the adsorbate.

In industrial settings, the dynamic adsorption of organic impurities holds significant importance. To study the adsorption process of phenol, a laboratory setup consisting of a 2.5 cm filter column and granulated GrSM-1 (fraction size: 0.5-2.5 mm) was utilised. The model solution used had a phenol concentration of 1.5 mg/dm<sup>3</sup>, representing the average concentration found at the inlet of an adsorption filter in a wastewater treatment system.<sup>15)</sup>

In the experiment, the loading layer in the column had a height of 20 cm and a weight of 54.38 g. The filtration speed employed was 3.5 m/h. At a concentration of 0.001 mg/dm<sup>3</sup>, the breakthrough point was observed, indicating the point at which the phenol concentration exceeded the permissible limit. The experimental results are visually depicted in Figure 2, which represents the dynamic adsorption breakthrough curve for phenol. The dynamic sorption capacity (DSC) and total sorption capacity (TSC) of “GrSM-1” were determined during the experiment and are presented in Table 6.



**Fig. 2:** The dynamic adsorption curve for phenol on GMCS under dynamic conditions was generated<sup>16)</sup>.

**Table 6.** Determination and measurement of the dynamic and total sorption capacities of GMCS.

Indicator, mg/g	Value	Volume of the passed water, dm³
DSC	4.8004	174.5001
TSC	6.8921	250.4041

Source: compiled by the authors.

Based on the Shilov equation, the GMCS layer exhibited a time duration ( $r$ ) of 95.2 hours and a coefficient of protective action ( $K$ ) of 612.6 hours/m. A proposal is being presented to integrate the GrSM-1 sorbent into the wastewater treatment system of “Aktobe Oil Refining” Limited Liability Partnership (LLP), with

the objective of enhancing both the technical and economic aspects of the system. During oil preparation, particularly in the dehydration and desalting processes, significant water consumption occurs. Oil is mixed with wash water in the pump room before entering the electro hydrators, where desalination and dehydration take place using electric current. The separated water is then discharged into a dedicated sewage network.

During the primary oil refining process, the oil undergoes several stages within Atmospheric Vacuum Tubulars (AVT) to produce light distillates and oil fractions. Following its passage through the electrical desalting plant, the oil is cooled and condensed using water in heat exchangers and condensers.<sup>17),18)</sup>

In AVT vacuum columns, water contacts oil vapours and gases in barometric condensers to create a vacuum for mixing. Unfortunately, this leads to contamination of wastewater with petroleum product vapours and hydrogen sulphide, which are harmful to metal processing equipment and not allowed in commercial petroleum products. To remove sulphur compounds like hydrogen sulphide, mercaptans, and phenols from the oil, it is washed with a caustic soda solution. This process transfers the sulphur compounds and other pollutants to the alkaline solution. Following multiple applications, the alkaline solution, containing a significant amount of sulphur compounds and pollutants, is eventually discharged into a designated sewer network. Refineries generate industrial storm sewage, which is released into the sewage system and undergoes treatment at wastewater treatment plants. Pollution sources encompass processed wastewater from condensation equipment and recovery tanks, which contain MEA solution. The chemical composition of the wastewater originating from “Aktobe Oil Refining” LLP is detailed in Tables 7-9.

**Table 7.** Characterization of wastewater from “Aktobe Oil Refining” LLP.

The name of indicators	Unit of measurement	Concentration	MPC
Hydrogen ions	pH units	7.33912	from 6.5 to 8.5
Dry residue	mg/dm³	2310.001	-
Total hardness	mg-eg/dm³	4.6023	-
Oil products	mg/dm³	10.814	from 0.1 to 5
SAS	mg/dm³	0.4903	0.5
Phenols	mg/dm³	5.0	0.001
Ammonia nitrogen	mg/dm³	5.5274	-
Common iron	mg/dm³	2.91901	from 2 to 20

Cadmium	mg/dm <sup>3</sup>	0.0001	from 0.01 to 0.6
Manganese	mg/dm <sup>3</sup>	0.25304	-

Source: compiled by the authors.

Table 8. Primary data for calculating the adsorption filter with GMCS loading.

Parameter	Value
Specific free volume (porosity), $\varepsilon$	0.40682
The density of wastewater $\rho_{ww}$ , kg/m <sup>3</sup>	1000.004
The coefficient considering the shape of particles, F	0.831
Loading height H, m	2.49
Kinematic viscosity coefficient of water (at 20°C), $\mu$	$1.004 \cdot 10^{-3}$
Number of filters, n	1
Filter performance $Q_{per}$ , m <sup>3</sup> /h (m <sup>3</sup> /s)	25 (0.0069)
Filter area $S_{ads}$ , m <sup>2</sup>	7.10002
Bulk density $\rho_n$ , kg/m <sup>3</sup>	670.0012
Filtering speed, m/h	3.4803

Source: compiled by the authors.

Table 9. The results of the calculation of the adsorption filter with GMCS loading.

Parameter	Value
Fictitious flow velocity $\omega_{fic}$ , m/s	0.0036
True flow velocity $\omega_{tr}$ , m/s	0.0089
Apparent density of the adsorbent $\rho_{app}$ , kg/m <sup>3</sup>	1129.8
Specific surface $a_v$ , m <sup>2</sup> /m <sup>3</sup>	1779
Reynolds number	17.7
Friction coefficient $\lambda$	12.4
Bulk layer pressure drop, Pa	613.8
Mass of GMCS for loading one adsorption filter, kg	15 242
Diffusion coefficient D, m <sup>2</sup> /s	$5.201 \cdot 10^{-10}$
Kinematic viscosity coefficient $\nu$ , m <sup>2</sup> /s	$1.004 \cdot 10^{-6}$
Diffusion Prandtl criterion	1930
Reduced diameter $d_{red}$ , m	0.0023
Mass transfer coefficient $\beta$ , m/s	$7.3 \cdot 10^{-6}$
Volumetric mass transfer coefficient $\beta_y$ , s <sup>-1</sup>	0.012

The proposed technological approach involves the incorporation of the hydrophobic granulated material GMCS into adsorption column in the wastewater treatment technology. The calculation focuses on the adsorption filter FSU 3.0-0.6, utilising the loaded sorption material GMCS. Table 8 provides the initial data employed for the calculation. Table 9 showed results of the calculation parameters using GMCS at the water purification in the wastewater treatment technology.

## 4. Discussion

The implementation of GMCS wastewater treatment technology has resulted in a significant reduction in pollutant emissions, amounting to 5.2 conventional tons per year.<sup>19),20)</sup> This reduction showcases the effectiveness of GMCS in removing pollutants from wastewater, preventing their release into the environment, and safeguarding the quality of water bodies. It contributes to environmental preservation, supports sustainable development, and maintains ecological balance. Its implementation allows industries to achieve environmental benefits, comply with regulations, and potentially realise financial advantages.

It is worth mentioning that several scientists have conducted similar studies, which require further examination to validate the discussed theory. N. Bukatenko and M. Zinchenko<sup>21)</sup> conducted a toxicological evaluation of spent detergent solutions with the objective of determining their level of hazard. The aim was to assess the potential risks associated with these solutions and their impact on the environment. The assessment results revealed that even with significant dilution of the used detergent solutions, their environmental safety could not be assured. This finding emphasises the persistence and potential harm of the components present in the waste detergent solutions, which can have adverse effects on ecosystems and organisms. Despite dilution, the hazardous nature of the solutions remained, indicating that the substances within them pose a risk to the environment even at lower concentrations. The results of the toxicological assessment underscore the need for effective waste management strategies and the implementation of environmentally friendly alternatives in detergent formulations. It is worth noting that only when improperly used water purification formulations, the result of purification virgin can indeed have negative indicators when considering the level of water purity.<sup>22-24)</sup> In the study conducted, with the correct process design and the use of carbonate sludge, the results were comforting for the further use of the treated water.

In a study conducted by B. S. Girgis and A.-N. A. El-Hendawy,<sup>25)</sup> the aim was to investigate the effects of phosphoric acid on the botanical structure of raw date kernels. The hypothesis proposed suggests that phosphoric acid triggers physicochemical transformations within the biomass by infiltrating the cell structure. This infiltration leads to particle swelling, partial dissolution of the biomass, breaking of bonds, and subsequent generation of novel polymeric structures that exhibit resistance to thermal degradation.<sup>26)</sup> The study further postulated that raw date kernels possess a low-porous and compact cell structure compared to other plant-derived raw materials. As a result, it was suggested that achieving the optimal effect of phosphoric acid treatment on raw date kernels might require higher concentrations of acid and/or elevated temperatures. This contrasts with the



conditions observed for other plant-derived raw materials, where the optimal effect is often achieved at lower temperatures. The findings from this study have significant implications for understanding the behaviour of raw date kernels under phosphoric acid treatment. The proposed physicochemical changes and the formation of new polymeric structures can potentially enhance the properties and thermal stability of the biomass. However, further research is needed to fully elucidate the underlying mechanisms and optimise the treatment conditions for raw date kernels.

M. Franz et al.<sup>27)</sup> conducted an investigation aimed at examining the influence of oxygen-containing groups, specifically carboxyl and carbonyl groups, on the adsorption of dissolved aromatic substances on ash-free activated carbon. The research aimed to gain a deeper understanding of how surface oxygen groups impact the adsorption capacity of the carbon material. The study's findings revealed that water adsorption, dispersion/repulsion interaction, and hydrogen bonding were the primary mechanisms through which surface oxygen groups influenced the adsorption capacity. These mechanisms played a crucial role in the interactions between the oxygen groups on the carbon surface and the dissolved aromatic substances.<sup>28),29)</sup> However, the study indicated that the donor-acceptor interaction had a minimal effect on the adsorption process. Additionally, the properties of the functional group present on the aromatic adsorbate were found to significantly influence the adsorption mechanism. Specifically, the hydrogen bonding ability of the functional group and its activating/deactivating effect on the aromatic ring played vital roles. These properties affected the strength of the interactions between the aromatic adsorbate and the surface oxygen groups on the activated carbon. This research holds significant importance, particularly in the development of suspension for water purification. Combining M. Franz's study with the current investigation could provide further insights into the specific applications of wastewater treatment in the future.

In the comprehensive research paper, G. Crini et al.<sup>30)</sup> delved into the fascinating realm of wastewater treatment to explore the potential of various adsorbents in removing pollutants. The study aimed to shed light on both conventional and non-conventional adsorbents and their effectiveness in tackling the ever-growing challenge of industrial wastewater pollution. One of the primary objectives of their investigation was to assess the prevalence and efficiency of conventional adsorbents commonly employed in wastewater treatment. Among these, activated carbon emerged as the most widely used and celebrated adsorbent in the field. In stark contrast to the popularity of conventional adsorbents like activated carbon, the researchers also turned their attention to exploring the potential of non-conventional adsorbents. These non-conventional materials, though possessing unique characteristics and properties, have not yet gained

mainstream adoption in wastewater treatment applications. Despite their promising attributes, the utilisation of non-conventional adsorbents has been relatively limited compared to their conventional counterparts.<sup>31)</sup> Their findings shed light on the need for further research and development to fully harness the potential of non-conventional adsorbents, given their untapped advantages and the imperative to explore sustainable alternatives in wastewater treatment. It is important to note that the use of non-conventional adsorbents has a place from the point of view of economy and convenience in production.<sup>32),33)</sup> It is also worth noting that it would be important to note the peculiarities of water purification using both conventional and non-conventional adsorbents.

M. A. Hubbe et al.<sup>34)</sup> conducted a comprehensive review focused on wastewater treatment methods applicable to Pulp and Paper (P&P) companies. The study aimed to provide these industries with cost-effective approaches to reduce the release of pollutants, such as biological or chemical oxygen demand, toxicity, solids, and colour. One key finding of their research is that the efficiency of water treatment can be significantly improved by implementing precise and rapid measurement techniques and employing critical treatment agents in factories.<sup>35)</sup> This approach has the potential to enhance the overall effectiveness of wastewater treatment processes in P&P companies.<sup>36)</sup> While this work proves to be valuable for the P&P sector, the researchers have not thoroughly explored the possibility of adapting similar technologies and methods for other types of industrial plants. As a result, the treatment options provided in the study might be limited in their applicability to other industries.

Based on an analysis of the sources, it can be concluded that the results of this study on the treatment of industrial wastewater from phenols using modified carbonate sludge are incomplete. This implies that there may be certain limitations or gaps in the results of the study that need to be addressed. It's important to note that the experiments were conducted using simulated wastewater with controlled phenol concentrations, which may not fully capture the complexities of real industrial wastewater. The study focused exclusively on one type of adsorbent, modified carbonate sludge, without exploring the potential of other low-cost alternatives. The lab-scale experiments, while informative, require validation at a larger scale to assess their feasibility for industrial applications, especially given the presence of various organic pollutants in actual industrial wastewater that could interfere with phenol adsorption. The adsorption mechanisms and chemical interactions between phenol and the modified carbonate sludge need a more comprehensive investigation, and the modifications made to the sludge should be further optimized to maximize adsorption performance. Therefore, a follow-up study is recommended to fill in the knowledge gaps based on the available data. This additional research can help develop

more effective and efficient methods for treating wastewater containing phenols, ultimately leading to improved environmental sustainability and better industrial practices.

## 5. Conclusions

To address the challenges posed by anthropogenic impact on the environment, a solution has been proposed: the utilisation of industrial waste for wastewater treatment. Specifically, the sorption material GMCS has been studied for its efficacy in treating wastewater and removing pollutants.

Based on experimental data, the adsorption efficiency of GMCS material in relation to phenol was determined. The results revealed an impressive efficiency of 99% in treating wastewater containing phenols under dynamic conditions. This high adsorption efficiency indicates that GMCS effectively captures and removes phenols from the wastewater, contributing to the overall purification of the water. In addition to the successful treatment of wastewater, the introduction of this proposed treatment technology offers significant ecological benefits. It has been calculated that the implementation of this technology leads to an ecological effect valued at 37.5 thousand dollars per year.

The ecological effect reflects the positive environmental impact achieved through the adoption of the proposed wastewater treatment technology. The monetary value assigned to this effect indicates the economic value associated with the environmental benefits obtained. The calculated value of 37.5 thousand dollars per year signifies the estimated financial savings or gains resulting from the reduced environmental impact and improved water quality. The calculated ecological effect of 37.5 thousand dollars per year demonstrates the tangible value and cost savings associated with implementing the proposed wastewater treatment technology. This economic aspect further underscores the viability and attractiveness of the technology, as it not only delivers environmental benefits but also offers potential financial gains or cost reductions.

In conclusion, the utilisation of GMCS as a sorption material for wastewater treatment presents an effective solution to mitigate anthropogenic impacts on the environment. The high adsorption efficiency of 99% for phenol removal and the calculated ecological effect of 37.5 thousand dollars per year highlight the positive outcomes and economic value of adopting this technology. By incorporating this wastewater treatment approach, industries and entities can simultaneously address environmental concerns, comply with regulations, and potentially realise financial benefits.

## References

- 1) Y. Masaki, "Characteristics of industrial wastewater discharged from industrialized provinces and specific

- industrial sectors in China based on the official statistical reports," *Evergreen*, **3**(2) 59-67 (2016). <https://doi.org/10.5109/1800873>
- 2) B.T. Sabarudin, S. Kartohardjono, "The combination of coagulation-flocculation and membrane processes to minimize pollution of tofu wastewater," *Evergreen*, **7**(1) 56-60 (2020). <https://doi.org/10.5109/2740942>
- 3) E.O. Ezugbe, S. Rathilal, "Membrane technologies in wastewater treatment: A review," *Membranes (Basel)*, **10** (5) 89 (2020).
- 4) S. Singh, V. Kumar, D.S. Dhanjal, S. Datta, D. Bhatia, J. Dhiman, J. Samuel, R. Prasad, J. Singh, "A sustainable paradigm of sewage sludge biochar: Valorization, opportunities, challenges and future prospects," *J. Clean. Prod.*, **269** 122259 (2020).
- 5) I. Radelyuk, K. Tussupova, K. Zhapargazinova, M. Yelubay, M. Persson, "Pitfalls of wastewater treatment in oil refinery enterprises in Kazakhstan - A system approach," *Sustainability*, **11** (6) 1618 (2019).
- 6) Farm water quality and treatment. (2014). [https://www.dpi.nsw.gov.au/\\_\\_data/assets/pdf\\_file/0/013/164101/Farm-water-quality-and-treatment.pdf](https://www.dpi.nsw.gov.au/__data/assets/pdf_file/0/013/164101/Farm-water-quality-and-treatment.pdf)
- 7) M. Yates, J. Blanco, M.A. Martin-Luengo, M.P. Martin, "Vapour adsorption capacity of controlled porosity honeycomb monoliths," *Microporous Mesoporous Mater.*, **65** (2-3) 219-231 (2023).
- 8) Sh. Kalam, S.A. Abu-Khamsin, M.S. Kamal, Sh. Patil, "Surfactant adsorption isotherms: A review," *ACS Omega*, **6** (48) 32342-32348 (2021).
- 9) J., Piekarski, K., Ignatowicz, T. Dąbrowski, "Analysis of selected methods use for calculation of the coefficients of adsorption isotherms and simplified equations of adsorption dynamics with the use of IZO application," *Materials (Basel)*, **14** (15) 4192 (2021).
- 10) T. Zamri, M. Munaim, Z. Abdul wahid, "Regression analysis for the adsorption isotherms of natural dyes onto bamboo yarn," *Int. J. Eng. Res. Technol.*, **4** (6) 1699-1703 (2017).
- 11) F. Mohamed Abdoul-Latif, A. Ainane, T. Hachi, R. Abbi, M. Achira, A. Abourriche, M. Brulé, T. Ainane, "Materials derived from olive pomace as effective bioadsorbents for the process of removing total phenols from oil mill effluents," *Molecules*, **28** (11) 4310 (2023).
- 12) G. Crini, E. Lichtfouse, "Advantages and disadvantages of techniques used for wastewater treatment," *Environ. Chem. Lett.*, **17** (1) 145-155 (2019).
- 13) The EU environmental implementation review 2022. (2022). <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52022SC0254>
- 14) L.A. Nikolaeva, N.E. Aikenova, "Adsorption Purification of Phenol-Containing Wastewater from Oil Refineries," *IOP Conf. Ser.: Mater. Sci. Eng.*, **1089** 012022 (2021).

- 15) M. Grosso, L. Biganzoli, F.P. Campo, S. Pantini, C. Tua, *Literature review on the assessment of the carbonation potential of lime in different markets and beyond*. Milano: Politecnico, 2020.
- 16) Y. Dehmani, A.A. Alrashdi, H. Lgaz, T. Lamhasni, S. Abouarnadasse, I.M. Chung, "Removal of phenol from aqueous solution by adsorption onto hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>): Mechanism exploration from both experimental and theoretical studies," *Arab. J. Chem.*, **13** (5) 5474-5486 (2020).
- 17) D.S.J. Jones, P.R. Pujadó, S.A. Treese, "Dictionary of abbreviations, acronyms, expressions, and terms used in petroleum processing and refining," in *Handbook of Petroleum Processing*, (2015). [https://doi.org/10.1007/978-3-319-05545-9\\_31-1](https://doi.org/10.1007/978-3-319-05545-9_31-1)
- 18) A.F. Ridassepri, F. Rahmawati, K.R. Heliani, J. Miyawaki, A.T. Wijayanta, "Activated carbon from bagasse and its application for water vapor adsorption," *Evergreen*, **7**(3) 409-416 (2020). <https://doi.org/10.5109/4068621>
- 19) R. Ferrentino, M. Langone, L. Fiori, G. Andreottola, "Full-scale sewage sludge reduction technologies: a review with a focus on energy consumption," *Water*, **15** (4) 615 (2023).
- 20) M. Kaur, N. Mittal, A. Charak, A.P. Toor, V. Singh, "Rice Husk derived Activated Carbon for the Adsorption of Scarlet RR an Anionic Disperse Dye," *Evergreen*, **10**(1) 438-443 (2023). <https://doi.org/10.5109/6782146>
- 21) N. Bukatenko, M. Zinchenko, "Environmental safety of waste detergent solutions," *Mater. Sci. Forum*, **1006** 202-207 (2020).
- 22) Z.A. Mansurov, J.M. Jandosov, A.R. Kerimkulova, S. Azat, A.A. Zhubanova, I.E. Digel, I.S. Savistkaya, N.S. Akimbekov, A.S. Kistaubaeva, "Nanostructured carbon materials for biomedical use," *Eurasian Chem.-Technol. J.*, **15** (3) 209-217 (2013). <https://doi.org/10.18321/ectj224>
- 23) A. Lyubchik, O. Lygina, S. Lyubchik, I. Fonseca, M. Tulepov, Z. Mansurov, S. Lyubchik, "Activated carbons from co-mingled liquid and solid organic wastes," *Eurasian Chem.-Technol. J.*, **17** 47-65 (2015). <https://doi.org/10.18321/ectj339>
- 24) S.B. Lyubchik, I.I. Perepichka, O.L. Galushko, A.I. Lyubchik, E.S. Lygina, I.M. Fonseca, Optimization of the conditions for the Cr (III) adsorption on activated carbon. *Adsorpt.*, **11** (5-6) 581-593 (2005). <https://doi.org/10.1007/s10450-005-5616-1>
- 25) B.S. Girgis, A.N.A. El-Hendawy, "Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid," *Microporous Mesoporous Mater.*, **52** 105-117 (2002).
- 26) B. Tyliczszak, A. Drabczyk, S. Kudłacik-Kramarczyk, "Smart, self-repair polymers based on acryloyl-6-aminocaproic acid and modified with magnetic nanoparticles—preparation and characterization," *Int. J. Polym. Anal. Charact.*, **23** (3) 226-235 (2018).
- 27) M. Franz, H.A. Arafat, N.G. Pinto, "Effect of chemical surface heterogeneity on the adsorption mechanism of dissolved aromatics on activated carbon," *Carbon*, **38** 1807-1819 (2000).
- 28) E.B. Asgerov, A.I. Beskrovnyy, N.V. Doroshkevich, C. Mita, D.M. Mardare, D. Chicea, M.D. Lazar, A.A. Tatarinova, S.I. Lyubchik, A.I. Lyubchik, A.S. Doroshkevich, "Reversible Martensitic Phase Transition in Yttrium-Stabilized ZrO<sub>2</sub> Nanopowders by Adsorption of Water," *Nanomater.*, **12** (3) 435 (2022). <https://doi.org/10.3390/nano12030435>
- 29) A.S. Doroshkevich, E.B. Asgerov, A.V. Shylo, A.I. Lyubchik, A.I. Logunov, V.A. Glazunova, A.Kh. Islamov, V.A. Turchenko, V. Almasan, D. Lazar, M. Balasoiu, V.S. Doroshkevich, A.I. Madadzada, Kh.T. Kholmurodov, V.I. Bodnarchuk, B.L. Oksengendler, "Direct conversion of the water adsorption energy to electricity on the surface of zirconia nanoparticles," *Appl. Nanosci.*, **9** (8) 1603-1609 (2019). <https://doi.org/10.1007/s13204-019-00979-6>
- 30) G. Crini, E. Lichtfouse, L. Wilson, N. Moran-Crini, "Conventional and non-conventional adsorbents for wastewater treatment," *Environ. Chem. Lett.*, **17** (1) 195-213 (2019).
- 31) A. Likhanov, A. Klyuvadenko, O. Subin, M. Shevchuk, M. Dubchak, "Gallic acid as a non-specific regulator of phenol synthesis and growth of regenerate plants of *Corylus avellana* (L.) H. Karst. and *Salix alba* L. in vitro," *Ukr. J. Forest Wood Sci.*, **13** (4) 52-63 (2022). [https://doi.org/10.31548/forest.13\(4\).2022.52-63](https://doi.org/10.31548/forest.13(4).2022.52-63)
- 32) B. Khussain, A. Brodskiy, A. Sass, K. Rakhmetova, V. Yaskevich, V. Grigor'eva, A. Ishmukhamedov, A. Shapovalov, I. Shlygina, S. Tungatarova, A. Khussain, "Synthesis of Vanadium-Containing Catalytically Active Phases for Exhaust Gas Neutralizers of Motor Vehicles and Industrial Enterprises," *Catalysts*, **12** (8) 842 (2022).
- 33) V.V. Tkach, M.V. Kushnir, S.C. de Oliveira, M.P. Zavhorodnii, O.A. Brazhko, M.M. Kornet, O.V. Luganska, V.V. Kopyika, Y.G. Ivanushko, M.P. Mytchenok, O.V. Ahafonova, P.I. Yagodynets', Z.O. Kormosh, L.V. Dos Reis, "The theoretical description for a sucralose electrochemical cathodical determination over a 9-9'-diacridyl-modified electrode," *Orbital*, **13** (3) 219-222 (2021).
- 34) M.A. Hubbe, J.R. Metts, D. Hermosilla, M.A. Blanco, L. Yerushalmi, F. Haghighat, P. Lindholm-Lehto, Z. Khodaparast, M. Kamali, A. Elliott, "Wastewater treatment and reclamation: A review of pulp and paper industry practices and opportunities," *BioResources*, **11** (3) 7953-8091 (2016).
- 35) A. Vakal, Yu. Lytvynenko, "Rare phytodiversity of the Ivotka river basin within the territory of the Sumy

- region,” *Ukr. J. Forest Wood Sci.*, **14** (2) 21-37 (2023). <https://doi.org/10.31548/forest/2.2023.21>
- 36) K. Syrmanova, A. Agabekova, S. Sakibayeva, A. Kovaleva, Y. Botashev, Z. Kaldybekova, S. Bayzhanova, “Physical-mechanical properties research of paint materials on the basis of petroleum bitumen,” *Egypt. J. Chem.*, **63** 609-616 (2020).