

## Intensification of the Wastewater Treatment Process of a Bitumen Plant with the Production of Recycled Water

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### ABSTRACT

The increasing demand for water with the industrialisation of the world is becoming a major problem as there is a water shortage all over the earth. Therefore, the water problem is one of the important problems that need to be effectively solved. This paper presents the results of research on wastewater treatment of bitumen production in the Mangystau region, which after physical and chemical treatment methods is sent to natural evaporation fields. As a result of research work, a method of wastewater treatment of bitumen plant was developed, which includes two stages: distillation of water on the solar plant and ozonation in order to oxidize volatile organic matter. Distillation to obtain primary treated water of 70–75% volume was carried out at 33–37 °C ambient temperature and 15–30 kPa rarefaction, at the same time COD of water was reduced by 68%.

**Keywords:** wastewater treatment, bitumen, oil, plant, distillation.

### INTRODUCTION

The growing need for water with the industrialization of the whole world becomes a serious problem, as there is a lack of water all over the Earth. Therefore, the water problem is one of the important problems that require an effective solution. One of the industries consuming a tonnage amount of water is the oil industry. The wastewater of the oil industry has a high pH >7, high BOD >30 mg/l and COD >125 mg/l and a high content of stable emulsions and suspended solids >30 mg/l. Traditionally, the wastewater from the oil industry is treated by using physical, chemical and biological methods. These methods cannot reduce the concentration of oil-containing products and ions of polluting elements to the standards provided for irrigation waters of melon crops or for watering green space of ornamental crops. Therefore, often the last stage of purification involves the discharge of water to the fields of natural evaporation, where water evaporation and accumulation of deposited salts occur, which are disposed of by known methods as they

accumulate. At best, it achieves the return of process water for reuse in production, while the return is 1–2 times, due to the accumulation of harmful components, which is undesirable for the technological process.

This article presents the results of a study of wastewater treatment of bitumen production in the Mangystau region, which, after physico-mechanical and physico-chemical treatment methods, is sent to the fields of natural evaporation.

The purpose of the study was to create a renewable water source with the production of treated wastewater that meets the requirements for landscaping, irrigation of public parks, green spaces. This technology is practiced in the United Arab Emirates, where 14% of the total volume of water resources corresponds to treated wastewater [Alsharhan et al., 2020].

In developed countries, treated wastewater has been widely used as a source of irrigation water for centuries. Purified recycled water is characterized by low cost, and has advantages in the content of trace elements, which helps to increase

crop yields and reduce dependence on chemical fertilizers. [Gamito et al., 1999].

It is proposed to treat wastewater by distillation on a solar desalinator created by the author's team [Koibakova et al., 2021; Kenzhetaev et al., 2019], followed by oxidation of volatile organic inclusions with ozone. The choice of a solar desalinator is based on the solar potential of the Mangystau region, where the number of sunny days is about three hundred per year, as well as a non-reactive method of water treatment to reduce the load on expensive chemical compounds and materials (membranes, ionites, sorbents, etc.).

Methods of reagent-free treatment of wastewater and oil-contaminated soils have been widely developed to reduce the burden on the ecosystem and technological costs in general for the production process. These include reverse osmosis [Talalaj 2015; Pervov et al., 2015], membrane distillation [Zhong et al., 2021; Ji et al., 2018; Gryta, 2020; Tong et al., 2019], nano-, ultrafiltration [Adib et al., 2015; Meng et al., 2015], and treatment with self-destructive air microbubbles [Agarwal et al., 2016].

Reverse osmosis plants for wastewater allowing purifying water from pollutants by 95% are commercially available, but due to the cost and high demand for electricity are not used in remote areas and in industry.

Membrane distillation technology is an advanced method of obtaining clean water and concentrating recyclable materials and provides virtually zero discharge of liquid after industrial wastewater treatment. Various studies have concluded that despite these advantages, energy efficiency remains a key factor for the future development of membrane distillation. In addition, wetting and contamination of the membrane is also a serious problem for desalination due to the high salinity and the presence of organic substances in the feed water [Zhong et al., 2021].

Moreover, nano and ultrafiltration methods require the use of expensive membranes, the payback of which for the purification of highly polluted waters seems almost impossible. Additionally, when purifying oil-contaminated waters, oily inclusions quickly form a hydrophobic layer that acts as a significant water barrier on the membrane surface, which reduces water flow, shortens the life of the membrane and increases energy consumption.

“Green” technologies using renewable energy sources have an advantage in all areas of waste

disposal and reclamation. The production of fresh water using solar desalinators is one of the sustainable ways to purify polluted and/or salty water. The reduction of COD from 85% to 98% from various industrial wastewater of the food industry, palm oil and oil production, water supply stations and municipal wastewater was shown. The degree of reduction of salt concentration in real seawater after evaporation in a solar distiller was 99.99%. Moreover, deep cleaning of oil-contaminated soils with the production of already cleaned soils was achieved on special solar installations [Arunkumar et al., 2022; Abdibattayeva et al., 2014; Abdibattayeva et al., 2021(a); Abdibattayeva et al., 2021(b)].

The method of obtaining fresh water by distillation at solar installations is often used for mineralized waters, where the impurity components are not volatile in the temperature range of 50–100 °C, but in the case of the presence of petroleum fractions in wastewater, it is necessary to combine the distillation method with subsequent oxidation.

The study of various advanced oxidation processes for wastewater treatment from the production of petroleum bitumen at different pH solutions for an effective oxidizer recommends ozone  $O_3$ , hydrogen peroxide  $H_2O_2$  and peroxene-a combination of ozone  $O_3$  and hydrogen peroxide  $H_2O_2$ . At a temperature of 25 °C, these oxidants provided a decrease in COD and  $BOD_5$  by 43% and 34%, respectively.

## THE EXPERIMENTAL PART

### Materials

The object of the study was the wastewater of a bitumen plant after a complex of treatment facilities, which is sent to the evaporation field of the following composition, mg/kg: 7.98 Li; 396 Al; 0.806 V; 0.725 Cr, 72.0 Mn; 409 Fe; 0.292 Co; 2.31 Ni; 6.23 Cu; 13.1 Zn, 0.286 As; 0.422 Se, 61.2 Sr; 15.9 Ba. Petroleum products – 0.84 mg/dm<sup>3</sup>; COD – 358.27 mg/dm<sup>3</sup>.

### Wastewater treatment methods

Wastewater treatment involves two stages (Fig. 1): distillation to solar desalinators (position 1–18) and oxidation of the distillate with ozone (position 19, 20). The solar desalination device

consists of: 1 – pump for wastewater intake; 2 – channels for heating wastewater with a helio-coating; 3 – lines for intake and supply of colder process water; 4 – branched branch pipe of pipes with a diameter of 50 mm for the supply of heated wastewater; 5 – channel with heated wastewater; 6 – channels of cold water drain; 7 – metal wall to increase the temperature in the volume of the desalination plant; 8 – vacuum pump; 9 – heat-insulated desalination fence; 10 – window opening; 11 – branched branch pipe of pipes with diameters of 50 mm for supplying colder process water to the surface of the condensate tank panel; 12 – corrugated panel-condenser for colder water; 13 – colder process water; 14 – colder process water discharge line; 15 – a condensate collector of a corrugated condenser; 16 – translucent double-slope heat-insulated coating with an air gap (10–12 cm); 17 – translucent heliopoating with a smooth inner surface; 18 – condensate collector desalination coating.

The method of wastewater treatment by desalination is carried out as follows. Water with the help of a pump – 1 is fed into the solar heating channel – 2 through the waste water intake line – 3 and at a temperature of 25–32 °C, the water is heated by solar energy to 55–63 °C, which is enough to condense it, due to the supply of colder water (artesian water with a temperature of 14–15 °C) and a decrease in pressure in the volume of the desalination plant.

As it heats up, water is fed through a heat-insulated branched branch pipe – 4 from pipes with a diameter of 50 mm into the channel – 5 of the desalination plant, where due to the temperature difference, water condenses on the lower surface of the “cold condenser” – 12. As the desalinated wastewater cools, it flows through the drain channel – 6 and further into the process

water channel. In parallel to the heated water, pump – 1 by means of nozzles – 11, cold water – 13 taken from the water utility is fed to the surface of the “cold” corrugated condenser – 12, to cool the desalination volume and achieve a state of saturation and condensation of moisture. The resulting condensate flows into the condensate collector – 15. The flow of cold water over the surface of the “cold” condenser is continuous to ensure the initial temperature, followed by its discharge in the same form into tap water through the discharge line – 14. On the inner surface of the heated translucent coating – 17, located above the surface of the “cold” condenser, moisture will also condense and collect in the condensate collector – 18. Translucent double-slope coating – 16 with an air gap of 10–12 cm, is heat-insulating and also as heat-insulated fences – 9, which helps to prevent heat loss from the influence of wind.

## RESULTS AND DISCUSSION

In the experimental solar desalination plant, work was carried out on desalination of wastewater with a volume of 4000 ml. After receiving desalinated (purified) water with a volume of 3000 mL, the operation of the solar desalinator was stopped, the volume of the cubic residue was 1000 mL. Tables 1 and 2 show the results of experimental work

The distillation flow and rate is directly proportional to the applied external pressure and temperature regime. At too high a pressure of 20–30 kPa, the transition of arsenic and selenium into distillate was observed, due to the possibility of volatility of organic arsenic

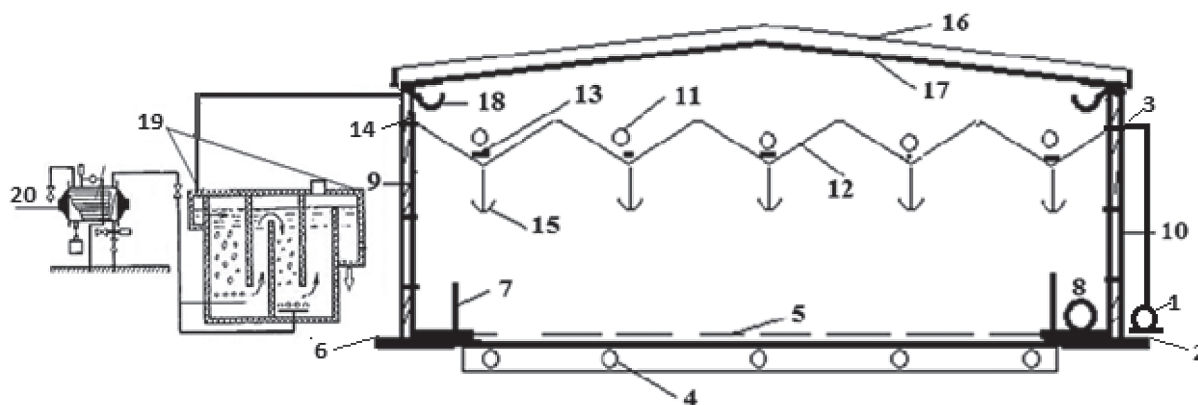


Figure 1. Wastewater treatment device

**Table 1.** Results of wastewater treatment in a solar desalination plant

No. experiment	Loaded, ml	t, °C environment	Distillation conditions				Received, ml	
			t, °C	P, kPa	P, mm. Hg	τ, min	Condensate	Remains
1	4000	37	70	30	225	120	3000	1000
2	4000	37	68	20	157	140	3000	1000
3	4000	38	70	15	112	160	3000	1000
4	4000	36	60	20	157	135	3000	1000
5	4000	33	55	15	112	128	3000	1000
6	4000	30	52	30	225	165	3000	1000
7	4000	30	51	20	158	165	3000	1000

**Table 2.** The results of chemical analyses of the obtained solutions

No.	Solutions	Mass fraction of elements. mg/L												
		Li	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	COD
1	I	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	0.08	0.06	181.5
	II	30.2	155	3.23	2.9	265	163	1.2	9.4	24.92	52.4	0.88	1.48	508.4
2	I	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	0.09	0.07	160.5
	II	30.6	154	3.22	2.9	265	163	1.2	9.6	26.1	52.7	0.67	1.36	504.4
3	I	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	<0.02	0.03	148.3
	II	32.0	154	3.22	2.9	265	163	1.2	9.6	26.1	52.7	1.1	1.42	514.4
4	I	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	<0.02	0.03	148.3
	II	31.4	154	3.22	2.9	265	163	1.2	9.6	26.1	52.7	1.12	1.42	514.4
5	I	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	<0.02	0.03	148.3
	II	30.5	154	3.22	2.9	265	164	1.2	9.6	26.1	52.7	1.12	1.44	514.4
6	I	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	<0.02	0.03	145.3
	II	31.4	154	3.22	2.9	265	166	1.2	9.6	26.1	52.7	1.12	1.42	524.2
7	I	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	<0.02	0.03	140.1
	II	31.4	154	3.22	2.9	265	166	1.2	9.6	26.1	52.7	1.14	1.42	519.0

I – desalinated (purified) water  
II – cubic remainder

compounds. If the pressure is too low below 15 kPa, the process slows down.

From the results of experimental data, it is recommended to desalinate wastewater at a solar installation at ambient temperatures of 30–37 °C and an external pressure of 15–20 kPa. The volume of purified water is 75% of the volume of the source water, the cubic residue is a source of rare metals like lithium and vanadium. When standing for more than 4 days, a brown precipitate containing 57–60% Fe<sub>2</sub>O<sub>3</sub> and 5–7% Mn, 0.1–0.2% As is observed. The COD values in the cubic residue due to concentration should have been higher than 700 mg/L, but due to partial oxidation when air enters during desalination, this indicator is lower than the calculated one. Due to the transition of the volatile fraction of petroleum products, the COD of the distillate obtained under recommended

conditions (experiments 3–7 of Tables 1 and 2) is 140–148 mg/L. In order to reduce the COD of water to the required level for watering green spaces no higher than 50 mg/L, work was carried out on the oxidation of water with hydrogen peroxide and ozone.

The use of hydrogen peroxide for water treatment and wastewater treatment attracts attention by the fact that this oxidizer, like ozone, does not change the salt composition of the treated water. The indirect effect of ozone on the process of alkaline deposition consists in the destruction of associated organic and other contaminants of the treated runoff, which can negatively affect the completeness of metal deposition. Such pollutants are some surfactants that cause colloidal stabilization of sediment particles, substances that form stable complexes with metal ions and are not subject

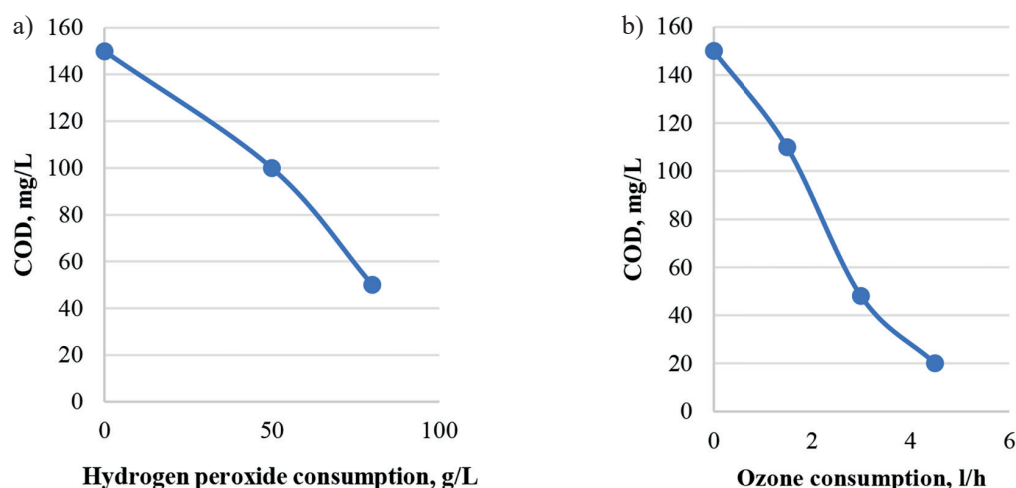


Figure 2. Effect of hydrogen peroxide and ozone consumption on reduction of COD values

to alkaline precipitation. Figure 2 shows the results of comparative data on the oxidation of petroleum products from distillate using hydrogen peroxide (a) and ozone (b).

The possibility of reducing the COD values in an oxidizing distillate using a solution of hydrogen peroxide and ozone was investigated. It was shown that the use of  $H_2O_2$  solution individually in dosages up to  $50 \text{ g/dm}^3$  of runoff does not contribute to a significant decrease in COD values. The greatest increase was observed with an increase in the consumption of hydrogen peroxide to 1.0–1.5%. A further increase in flow rate at one stage is ineffective.

From an economic point of view, its use for wastewater treatment is most effective where it is a by-product of any technological process. Moreover, the choice of disinfection method is determined not only by technical and economic indicators, but also by environmental requirements. One of the “environmentally friendly” wastewater treatment technologies is the ozone treatment technology.

The optimal ozone consumption for reducing COD values to a sanitary and hygienic value is 3 liters/hour, which corresponds to 48 mg/L of COD.

In accordance with sanitary and hygienic and veterinary requirements, it is allowed to grow industrial crops, cereals for fodder, fodder, tree and shrub, including decorative and protective plantings, on lands irrigated with wastewater. Irrigation of vegetables, melons and berry crops with sewage is not allowed.

To control the quality of water during its further use when watering green spaces under laboratory conditions, the irrigation of melon crops with purified water was tested, the development of roots by sowing beets, cucumbers and oat grains into the soil and watering them was investigated. The results of the preliminary experiment are presented in Table 3. In authors’ practice, 30 plants for each type of water have been sown for 10 weeks, that is, stops were made at one plant every week. In the study, 50 mL of water was poured every 3 days.

As a result of the experiment, the inhibition of the development of cucumbers and oats of crops

Table 3. The effect of purified water on the vital activity of melons

Irrigation water	Melon crops	Average length of melons roots. mm ( $L_{cp}$ ). mm	Test reaction	Braking coefficient $E_B$ . %
Drinking water	Beet	6.70	Norm	-
	Cucumber	7.50	Norm	-
	Oats	6.70	Norm	-
Purified water from bitumen plant effluents	Beet	5.8	Braking	13.43
	Cucumber	6.64	Braking	11.4
	Oats	6.70	Norm	0.00
Source wastewater of the bitumen plant	Beet	4.4	Braking	34.32
	Cucumber	5.6	Braking	25.33
	Oats	5.3	Braking	20.89

grown with irrigation with distilled water of a bitumen plant is observed. For cucumbers, the braking coefficient of BC = 11.4%, for beetroot BC = 13.43%, but these indicators are below the maximum permissible phytotoxicity index below 20%. Therefore, water obtained by desalination in a solar installation and purified with ozone from oil residues is not considered dangerous or toxic in terms of phytotoxicity.

After seven weeks, examinations were conducted to determine the ability of plants to accumulate the chemical elements in their composition.

Since there were the first experiments, all parts of plants – roots, stems, leaves – were taken as one sample. In the drying cabinet, the plants were dried to a constant mass of 50–60 °C, and then turned into ash by burning in a muffle furnace at 500–550 °C, the ash content of the cucumber plant is 15%, the ash content of the oat plant is 7.2%, whereas the ash content of the beet culture is 3.5%. After the unburned residue was completely transferred to the solution in soda and alcohol solutions, the content of heavy non-ferrous metals in the solution was determined.

The content of heavy and non-ferrous metal ions in the unburned residue of all plant crops is below 0.01%. This indicator of the result is that the purified water contains a low content of heavy and non-ferrous metals.

The main purpose of this experiment is to test the ecotoxicity of the composition of the grown plants and determine the degree of their influence, if a positive result is achieved in the experiment, we will use industrial wastewater for growing garden plants in the future.

## CONCLUSIONS

As a result of research work, a method for wastewater treatment of a bitumen plant has been developed, which includes two stages: water distillation at a solar installation and ozonation for the purpose of oxidation of volatile organic substances. Distillation to obtain primary purified water of 70–75% of the volume was carried out at ambient temperature of 33–37 °C and a discharge of 15–30 kPa, while the COD of water decreased by 68%. The content of non-ferrous metals and toxic elements such as arsenic is at the level according to GOST 17.1.1.04-80 for irrigation water of melons. The reduction of COD values with the use of ozone proceeds more efficiently

than with the use of hydrogen peroxide from an economic point of view. Moreover, the choice of disinfection method is determined not only by technical and economic indicators, but also by environmental requirements.

One of the “environmentally friendly” wastewater treatment technologies is the ozone treatment technology. The optimal ozone consumption for reducing COD values to a sanitary and hygienic value is 3 liters/hour, which corresponds to 48 mg/L of COD.

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