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Coke-Chemical Plants Wastewater Treatment Processes

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Abstract

In this work the issue of treatment of coke plant wastewater. The aim of this work was to study environmental pollution caused by emissions and effluents of coke plants to develop technologies to prevent penetration of hazardous substances into the water basin. Field studies were conducted, and the main sources of pollution, their chemical composition and concentrations were determined. In addition, mechanism of adsorption purification of effluents from particularly hazardous chemicals were developed.

Keywords: Coke wastewater; Environmental pollution; Adsorption; Layered double hydroxides; Sorption technologies

Introduction

Environmental protection, sustainable development, and habitat preservation are the most important issues now [1-5]. The problems of neutralization and utilization of industrial wastewater and its treatment are of extreme importance. New industrial effluents constantly appear in the world and require dedicated study. Wastewater from manufacturing plants, released into the surrounding ecosystem, may cause irreparable damage to the environment.

Industrial enterprises are the main source of environmental problems related to wastewater discharge. One of the key factors of wastewater pollution from chemical plants is the use of inefficient treatment facilities. Treatment of industrial wastewater requires new technologies that can minimize the negative impact on the environment [6-12].

Dniprovskyi coke plant is one of the oldest chemical plants in the Ukraine, which production began as early as 1931. The plant specializes in the production of coke, tar and ammonium sulfate. The plant's equipment is severely outdated, and there has been no modernization in the past 30 years. Noteworthy that this chemical plant is located on the banks of the Dnieper River, which is the largest river in the country. The wastewater from the plant is discharged directly into the river.

The following objectives were set prior conducting the study:

1. Study of chemical composition of the plant wastewater.
2. Study of chemical composition and physic-chemical properties of the bottom sediments of the Dnieper River waterfront.
3. Development of methods and technologies to reduce the hazardous impact on the environment.

Since the plant is located on the river shore, there is a constant pollution of the river via both authorized and illegal discharges of industrial waste (Figure 1). Field studies revealed that the maximum negative impact is caused by discharges from the intermediate naphthalene tank - a chemical waste accumulator - tarry sediments accumulated over decades in the river near the plant.

The facility that pollutes the river the most is the drain from the naphthalene interceptor tank, which is located at the very edge of the plant, on the bank of the river (Figure 2). The naphthalene vessel is a vertical cylindrical concrete tank originally designed to accumulate wastewater, mostly with high naphthalene content. For some unknown reason, the underground part of the tank cracked. Water with the high concentration level of naphthalene and other components began to overflow through the underground pipe into the bay. The most frequent overflows occur during heavy rainfall, meaning the tank also receives drain sediments.

Materials and Methods

Ion-selective electrodes were used to determine cation and anion concentrations. Gas-liquid chromatography was used to determine the concentrations of organic substances. Prior analysis, the organic substances were extracted from the aqueous and resin layers using sulfuric ether. Most of the layered double hydroxides (LDH) were obtained by co-precipitation via addition of the solution containing NaOH and Na_2CO_3. To obtain LDHs with counterions other than carbonate ions, the latter were replaced by ion exchange in a nitrogen atmosphere. Matrix synthesis was used to synthesize LDHs with the targeted lattice spacing values. The structure and chemical composition of LDHs was determined via X-ray diffraction analysis.

Figure 1: Illegal discharges of industrial waste.

Figure 2: Drain from the naphthalene tank.

Results and Discussion

Study of industrial effluents

The sample taken from the naphthalene tank, after sedimentation was divided into two layers - the bottom aqueous layer and the top organic layer. Chemical analysis showed that the organic layer has the following composition: naphthalene - 64.22%; indene - 7.31%; o-xylene - 0.54%. In addition, there are methylstyrene, toluene, thiophene, methylthiophene, ethylbenzene and heavy oils present in the amount of 22.06%.

The content of organic matter in the effluent from the naphthalene tank fluctuates within a wide range between 0.02 and 0.81%. The component composition of bottom sediments in the adjacent waterfront of the river was studied. Samples of a viscous black liquid with a pronounced naphthalene odor were taken from the bottom of the bay. The water content in these samples is about 59.1% on average. The total content of petroleum products is 0.95mg/l, which is twenty times higher than standard. Gas chromatography analysis showed the following results: naphthalene - 8.11%; anthracene - 7.42%; acenaphthene - 7.19%; fluorene - 7.01%; phenanthroline - 6.38%; indene - 2.74%; the rest was unidentified. For inorganic compounds, there was a 30-fold excess for nitrogen; a 10-fold excess for surfactants; and a 20-fold lack of oxygen. One of the hazardous objects that pollutes the river is a chemical waste reservoir. The reservoir is overfilled, and during heavy precipitation the liquid flows into the ravine and drains into the river (Figure 3). The reservoir contains about 60 thousand tons of tarry products and about 150 thousand cubic meters of polluted water. The main pollutants are rhodanides, phenols, and petroleum products.

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Figure 3: Drain into the river.

Development of wastewater neutralization technologies

Realizing that it was impossible to solve all problems at once, it was decided to start by removing naphthalene from the effluent from the intermediate tank. Thus, we developed an adsorption technology using LDHs. LDHs is a class of inorganic compounds composed of positively charged layers of metal hydroxides as well as anions and solvate molecules in the interplanar space. The hydroxides form a structure of octahedral cavities filled with metal cations [13-18].

LDHs are capable of exchanging anions, both organic and inorganic. A general formula of LDHs is $[M^{n+}_{1-x}M^{m+}_{x}(OH)_{z}]^{q+}(A^{l-})_{q/l.}$ pH_2O, where M^{n+} и M^{m+} are metal cations, which form a hydroxide matrix. The most abundant LDH is $[Mg_x Al_y (OH)_z]$.

The lattice spacing of LDHs can be adjusted from 4.6 up to 50 Å. The development of naphthalene effluent removal technology was carried out according to the maximum concentration of naphthalene. The maximum concentration value of 0.81% was chosen for the calculations. Moreover, due to comparable size and structure of the polycyclic aromatic molecules of naphthalene $C_{10}H_8$ and indene C_9H_8, the adsorption process for both hydrocarbons can be done using $Mg_4Al\text{-}CO_3$ with lattice spacing of 7.91 Å.

The volume of effluent from the naphthalene tank is on average 10 liters per hour. The first suggestion was to fill the tank with concrete to eliminate the cracked bottom. However, this proposal was rejected, because it was not clear where the naphthalene water would break through in future, and it was decided to carry out sorption treatment. Model experiments were performed to evaluate the sorption process of contaminants using LDHs. In principle, 1g of LDH adsorbs about 1g of aromatic compounds. The solubility of aromatic compounds in water is very low: naphthalene and styrene – 30mg/L, xylene – 15mg/l, methylstyrene – 10mg/l. For example, only 1g of naphthalene can be dissolved in 30liters of water.

To study selectivity of adsorption, 10g of LDHs were poured into water containing equal concentrations of aromatic substances (naphthalene, p-xylene, indene, alpha-methylstyrene) and repeatedly washed. Noteworthy, their concentrations were higher than the solubility limit. After washing and drying, the sample was extracted with sulfuric ether. The amount of adsorbed aromatic compounds was 0.8g/l. Chromatographic analysis revealed the following component distribution: naphthalene - 52%; indene - 37%; p-xylene - 10%; alpha - methylstyrene - less than 1%. One can conclude the presence of aromatic rings facilitate adsorption. As for alpha-methylstyrene, its benzene ring has higher electron density than the unsubstituted benzene, and its vinyl fragment of the is depleted. Thus, the methyl group does not change the electron density distribution of the aromatic ring, but blocks neighboring active centers of LDHs.

Below is the estimation of required amount of LDHs for naphthalene sorption. 1 liter of water from the naphthalene vessel may contain up to 30 mg of naphthalene. LDHs can adsorb up to 0.8g of naphthalene dissolved in 26 liters of water. Considering the wastewater rate of 10 liters per hours, 1g of LDH sorbent may last about 2.5 hours (or 10g of LDH per day). At such a consumption rate of sorbent it is not feasible to install adsorbers working in parallel; it is rather enough to replace the sorbent once every 6 months. An alternative technology was used to dispose of the chemical waste reservoir. Aqueous and resin layer samples were taken for analysis. The results showed that the aqueous layer contains 6.3mg/l of sulfates, 1.5mg/l of rhodanides, 0.18mg/l of cyanides, 0.09mg/l of pyridine and 0.09mg/l of naphthalene. Its pH is 4. The concentration of substances that may phase transfer from the resin layer to water was also studied: petroleum products– 2.15mg/l, phenols – 1.13mg/l. The chemical analysis showed presence of naphthalene of 17.1%; phenol – 17.1%; sum of phenanthrene and anthracene – 15.2%; biphenyl – 9.66%; fluorene – 2.53%, α-methylnaphthalene – 1.93%; indene – 0.85%. Based on the pH value of 5 for the aqueous extract in terms of

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sulfuric acid, it takes 75g of Ca $(OH)_2$ per kg of the resin layer. Considering the waste of 60 thousand metric tons, the total required amount of calcium hydroxide is:

0.75g/kg. 60 000 000kg = 45 000 000g = 45 metric tons.

Based on the pH level of 4 for the aqueous extract in terms of sulfuric acid, it takes 7.5g of Ca $(OH)_2$ per liter of the aqueous layer. Considering the total volume of 150 thousand cubic meters of waste, the total required amount of calcium hydroxide is:

7.5g/l. 150 000 000 l = 1125 000 000g = 1125 metric tons

The concentration of phenols in the aqueous layer of the accumulator is 0.027g/l. Thus, the total amount of phenol is:

0.027g/l = 27g/m^3. 150 000m^3 = 4.05 metric tons.

Considering the value of exchange capacity of E = 0.46meq/g, complete adsorption of phenols requires 93 metric tons of sorbent:

4050: 0,46. 10^{-3}. 94 = 93t

As a result, 93 metric tons of LDH and 1179 tons of calcium hydroxide are required for complete neutralization of the chemical waste in the accumulator. Once the neutralizing agents are poured into the storage tank, it can be turned into a pond and planted with algae.

Conclusions and Perspectives

The following conclusions were made based on the a fore mentioned results. Dniprovskyi coke plant has a negative impact on the environment, polluting the Dnieper River with hazardous chemicals – naphthalene, phenol and other chemical substances.

The main sources of pollution are discharges from the naphthalene tank and the accumulator of liquid chemical waste. Removal of aromatic substances such as naphthalene, indene and others are possible with the help of LDH sorbents. Removal of the chemical waste accumulator can be carried out with the help of sorption technologies.

Author Contributions

Writing-original draft preparation and supervision, writing-review and editing, supervision, E.B. and A.K. All authors have read and agreed to the published version of the manuscript.

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