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ELECTROCHEMICAL TREATMENT OF AIRPORT RUNOFF WATER CONTAINING ETHYLENE GLYCOL

[1]D.Sh. Magomedova, [2]Z.M. Alimirzayeva, [1]A.G. Magomedova
[1]A.B. Isaev, [3]T.A. Kharlamova

[1]Department of Inorganic Chemistry and Chemical Ecology, Daghestan State University, M. Gadjieva, 43a. Makhachkala, Russia.
[2]Department of General and Biological Chemistry, Daghestan State Medical University, sq. Lenina, 1. Makhachkala, Russia, 367000.
[3]Department of Theoretical and Applied Chemistry, Moscow State Regional University, Vera Voloshina str., 24. Mytishchi. Moscow region, Russia, 141014. E-mail: harlamova_tanya@list.ru

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***Abstract**: Airports are one of the sources of environmental pollution with runoff water containing emerging contaminants. The process of electrochemical purification of model runoff water containing ethylene glycol and formed during the treatment of aircraft with anti-icing agents was studied. As an anode there was used PbO_2 electrode. The structure and morphology of PbO2 electrode samples obtained by electrochemical deposition on the titanium plate surface was studied using scanning electron microscopy. It revealed that the use of PbO_2 as an anode makes it possible to bring the COD value of the solution to the required standards. After electrolysis, the COD values for all studied ethylene glycol concentrations from 10 to 100 mg/l were in the range of 0.34-4.6 mgO2/l. The effect of current density, concentration of ethylene glycol and sodium chloride on the efficiency of electrochemical oxidation of ethylene glycol was analyzed.*
***Keywords**: runoff water, ethylene glycol, airport, oxidation, electrochemical, lead dioxide.*
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Introduction

Pollution of water with organic contaminants is the most important problems that many researchers have recently been trying to solve to ensure and maintain the state of water quality [1-3].

In order to prevent the pollution of aquatic ecosystems with organic contaminants, wastewater from various industries is currently subjected to preliminary treatment using various methods before being reset [4].

Airports are one of the sources of environmental pollution [5], associated with the treatment of aircraft with anti-icing agents, cleaning and maintenance of aircraft, ground service equipment and vehicles. This uses a significant amount of harmful chemical compounds that enter the runoff water. Pollutants in airport runoff water have the organic and inorganic nature, among which ethylene glycol can be noted as one of the toxic compounds [6, 7].

Electrochemical methods are considered to be the most promising for removing organic pollutants from wastewater [8–10]. Oxidation of contaminants in an electrochemical cell is achieved either through direct electron transfer to the anode, or through indirect or mediated oxidation [11]. The studies presented in [12] showed that the nature of the electrode material has a great influence on both the selectivity of the process and the efficiency. For example, on some anodes, only partial oxidation occurs and they are used for the electrochemical conversion of pollutants, while on others, the compounds are completely mineralized to CO_2 (electrochemical combustion) [13].

Regardless of the anode material, the first step in the oxygen transfer reaction is the

discharge of water molecules to form an adsorbed hydroxyl radical (HO). The nature of the material determines the "activity" and "inactivity" of the electrodes. On "active" electrodes, adsorbed radicals interact so strongly with the anode to form chemisorbed "active oxygen" or oxide, provided that higher oxidation states are available to the electrode material. The surface of the redox couple MO/M (chemisorbed "active oxygen") can act as an agent in the process of oxidation or electrochemical transformation of organic compounds on the surface of "active" electrodes [14, 15].

Lead dioxide with a high O_2 overvoltage is one of the most commonly used anodes for the removal of organic compounds [16, 17]. Based on this, in this work, we consider the electrochemical oxidation of ethylene glycol on PbO_2 deposited on the titanium plate surface.

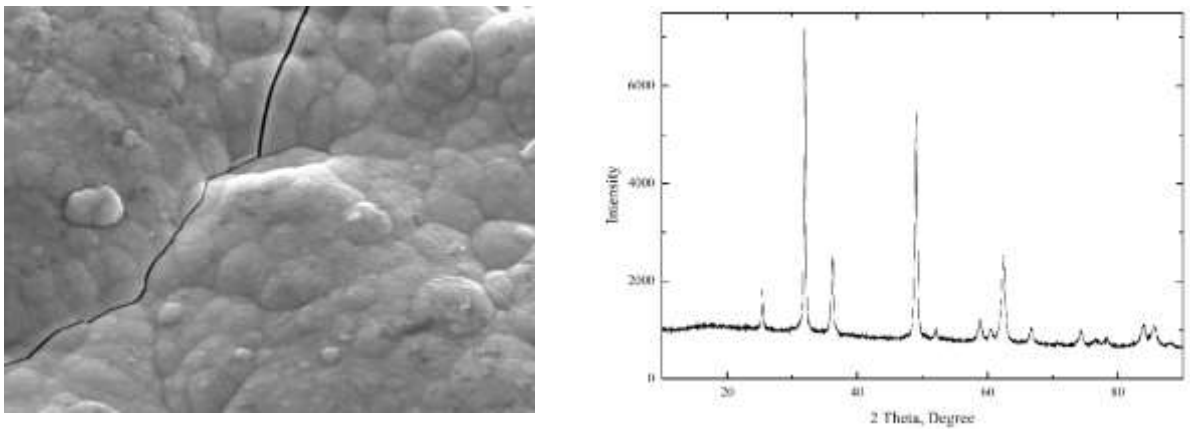
Experimental

In order to prepare the PbO_2 electrode, a titanium plate was preliminarily subjected to ultrasonic treatment for 3 h in distilled water. Then the titanium plate was placed in a sodium hydroxide solution for 30 min, followed by treatment in a hydrochloric acid solution. The treated titanium plate was placed in acetone. Then PbO_2 was deposited using a 0.25 M $Pb(NO_3)_2$ solution containing 0.01 M NaF and 0.1 M HNO_3 solution. Electrolysis was carried out at a voltage of 3–4 V during the day [18]. The obtained Ti/PbO_2 electrode was washed in distilled water and dried for further use. Electron microscopy and XRD analysis were used to characterize the resulting electrode. An image of the electrode surface was obtained using a scanning electron microscope (JEOL JSM_7001F (Japan)). XRD analysis was carried out on a PANalytical Empyrean series 2 diffractometer.

Ti/PbO_2 electrode was used as an anode for electrolysis. A titanium plate was used as a cathode. 100 ml of ethylene glycol solution with various concentrations was poured into the cell for electrolysis. The content of ethylene glycol was followed by a decrease the COD of the solution using a fluid analyzer "Fluorat-02-3M" (Russia).

Results and discussion

The structure and morphology of Ti/PbO_2 electrode samples obtained by deposition on the surface of a titanium plate was studied using scanning electron microscopy



a) b)

Fig. 1. SEM image (a) and XRD pattern (b) of the Ti/PbO_2 electrode sample.

As can be seen from Fig. 1a, the surface of the titanium plate is covered with a continuous layer of PbO_2. The slight roughness of the PbO_2 surface is apparently related to the layer-by-layer deposition of PbO_2 on titanium plate. Fig. 1b shows the XRD pattern which is accord with the obtained PbO_2 film. The ICDD PDF4 database was used to identify the peaks in the XRD pattern. The peaks on the XRD pattern correspond to lead dioxide, which is confirmed by their identity to the data for PbO_2 in the database (98-003-4234).

The electrochemical oxidation of ethylene glycol in a two-electrode cell, where a Ti/PbO_2 electrode was used as an anode and a titanium plate as a cathode, was carried out. Fig. 2 shows the COD of an ethylene glycol solution on the electrolysis time at various current densities. As the current density increases, the rate and efficiency of the electrochemical oxidation of ethylene glycol increase.

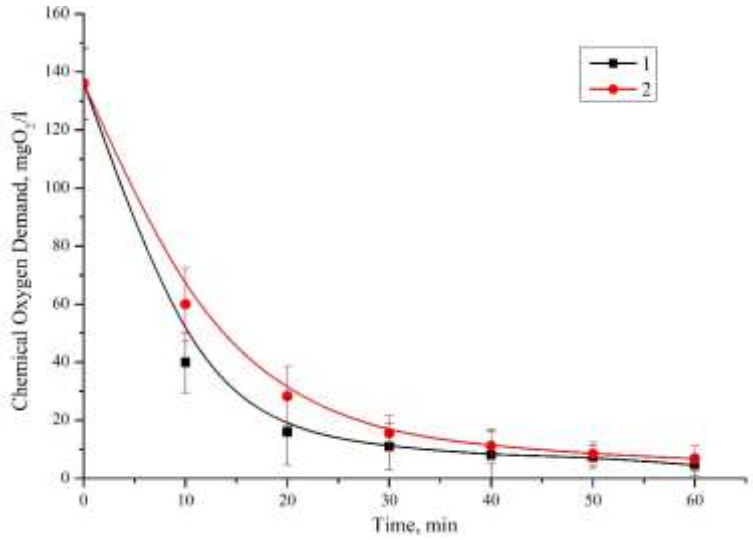


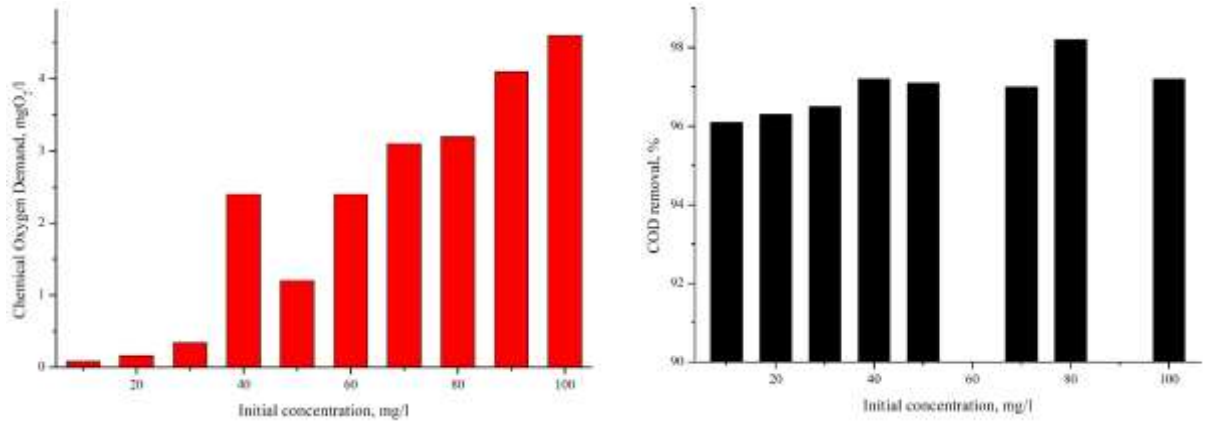
Fig. 2. COD of ethylene glycol solution from electrolysis time at different current densities (A/cm^2): 0.013; 2 - 0.006 (0.1 M NaCl, C (ethylene glycol) = 100 mg/l, Q=0.325 Ah.)

As can be seen from Fig. 2, at a current density of 0.013 A/cm^2, COD is completely removed already after 15 minutes of electrolysis. A twofold decrease in the current density leads to a significant increase in the electrolysis time until the COD is completely reduced. The amount of electricity was 0.325 Ah.

The concentration of ethylene glycol in the solution significantly affects the COD index. With an electrolysis time of 10 minutes, the COD value of the solution is 5.92 mgO_2/l, which corresponds to the “dirty” water category.

The electrochemical treatment of the ethylene glycol solutions makes it possible to reduce COD to values for very pure waters. On fig. 3 (A) shows the dependence of the residual COD for ethylene glycol solutions on its initial concentration. After electrolysis, the COD values for all studied ethylene glycol concentrations were in the range of 0.34-4.6 mgO_2/l. Thus, the electrochemical treatment of aqueous solutions of ethylene glycol using sodium chloride as an electrolyte makes it possible to bring the wastewater performance to the required standards.

The concentration of ethylene glycol in the solution has no significant effect on the degree of purification (Fig. 3 (b)). When the concentration of ethylene glycol changing in the range from 10 mg/l to 100 mg/l, the degree of COD reduction ranges from 96 to 98%. The effect of the concentration of sodium chloride on the degree of ethylene glycol removal was also investigated.



a b

Fig. 3. COD of aqueous ethylene glycol solutions after electrolysis depending on its initial concentration (a) and the effect of ethylene glycol concentration on the efficiency of electrochemical purification (b)

Fig. 4 shows the effect of the degree of ethylene glycol removal on the concentration of sodium chloride. An increase in the sodium chloride concentration leads to an increase the degree of runoff water purification from ethylene glycol. At a sodium chloride concentration of 0.15 M, the degree of ethylene glycol removal reaches 99.1%. The increase of the degree of ethylene glycol removal with an increase of the sodium chloride concentration is associated with a more intense formation of active chlorine in the solution, which approaches the optimal value at sodium chloride concentrations in the solution corresponding to 0.15 M.

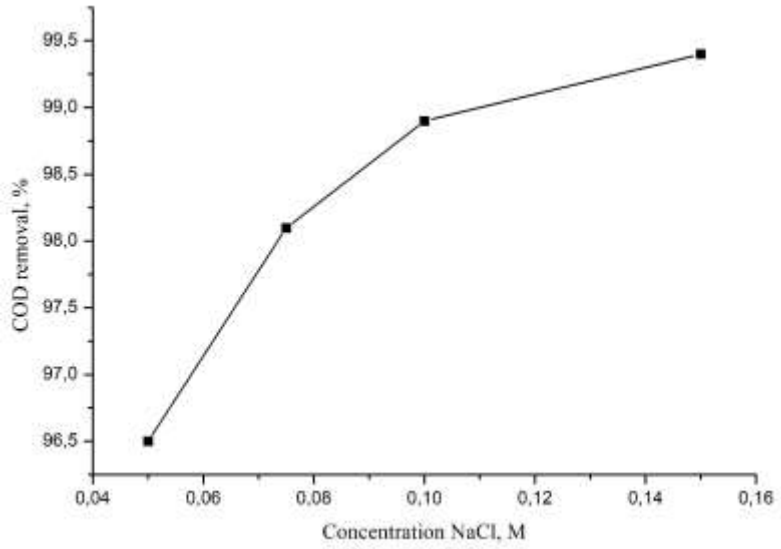


Fig. 4. Effect of sodium chloride concentration on the efficiency of electrochemical cleaning of solutions from ethylene glycol ($C_{ethylene\ glycol}$ =75 mg/l)

Thus, the electrochemical oxidation of ethylene glycol in a solution of sodium chloride increases the efficiency of the process with an increase in the concentration of sodium chloride, which is associated with the generation of active chlorine and indirect oxidation of ethylene glycol. The study of the effect of current density on the degree of ethylene glycol removal at the same concentrations of sodium chloride and ethylene glycol revealed that the

optimal current density was 0.1 A/cm^2. An increase of the current density leads to the appearance on the cathode surface of the polymer film of the of ethylene glycol reduction products and the products of its oxidation. At higher current densities, an intense evolution of oxygen and hydrogen is observed, while a decrease in the degree of purification of the solution from ethylene glycol by 10–15% is also observed.

Conclusion

The influence of the ethylene glycol concentration to the water COD value was investigated. It found that at an ethylene glycol concentration of 100 mg/l, the COD value of the solution is 5.92 mg O_2/l which corresponds to the "dirty" water category. It established that the electrochemical treatment of aqueous solutions of ethylene glycol using sodium chloride as an electrolyte makes it possible to bring the wastewater indicators to the required standards and the COD values for all studied ethylene glycol concentrations lie in the range of 0.34-4.6 mg O_2/l. It revealed that at the same concentrations of sodium chloride and ethylene glycol, the optimal value of the current density at a degree of purification of 99% was 0.1 A/cm^2.

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HAVA LİMANLARININ TULLANTI SƏTH SULARLARININ ETİLENQLİKOLDAN ELEKTROKİMYƏVİ TƏMİZLƏNMƏSİ

[1]D.Ş. Maqomedova, [2]Z.M. Alimirzayeva, [1]A.G. Magomedova
[1]A.B. Isaev, [3]T.A. Xarlamova

[1]Dağıstan Dövlət Universiteti
M.Hacıyev küç., 43a. Maxaçqala 367001. Rusiya
[2]Dağıstan Dövlət Tibb Universiteti
Lenin pr.,1, Maxaçqala 367000. Rusiya
[3]Moskva Dövlət Regional Universiteti
Vera Voloşina küç., 24, Mıtişı, 141014. Rusiya, E-mail: harlamova_tanya@list.ru

Xülasə: *Hava limanları ətraf mühiti tullantı suları ilə çirkləndirən mənbələrdən biridir. Təyyarələrin donması əleyhinə reagentlərdən istifadə nəticəsində etilenqlikol əmələ gəlir və tullantı sularına daxil olur. Bu işdə tərkibində etilenqlikol olan model tullantı səth sularlarının elektrokimyəvi təmizlənməsi tədqiq edilmişdir. Anod kimi PbO_2 əsaslı elektroddan istifadə olunub. Göstərilmişdir ki, bu anoddan istifadə etməklə elektrolizdən sonra məhlulda etilenqlikolun miqdarı 0.34-4.6 mq O_2/l təşkil edir, bu da müəyyən edilmiş norma daxilindədir.*

Açar sözlər: *tullantı suları, etilenqlikol, sularların elektrokimyəvi təmizlənməsi, anod*

ЭЛЕКТРОХИМИЧЕСКАЯ ОЧИСТКА ПОВЕРХНОСТНЫХ СТОКОВ ТЕРРИТОРИЙ АЭРОПОРТОВ, СОДЕРЖАЩИХ ЭТИЛЕНГЛИКОЛЬ

[1]Д.Ш. Магомедова, [2]З.М. Алимирзаева, [1]А.Г. Магомедова, [1]А.Б. Исаев, [3]Т.А. Харламова

[1]Кафедра неорганической химии и химической экологии, Дагестанский государственный университет. ул. М. Гаджиева 43а. г. Махачкала, 367001. Россия.
[2]Кафедра общей и биологической химии, Дагестанский государственный медицинский университет Министерства здравоохранения Российской Федерации.
пл. Ленина, 1. г. Махачкала, 367000. Россия
[3]Кафедра теоретической и прикладной химии,
Московский государственный областной университет,
ул. Веры Волошиной, д.24. г. Мытищи. Моск. обл. 141014. Россия

***Аннотация**: Аэропорты являются одним из источников загрязнения окружающей среды сточными водами. Исследован процесс электрохимической очистки модельных сточных вод, содержащих этиленгликоль и образующихся при обработке самолетов противообледелительными реагентами. В качестве анода был использован электрод на основе PbO_2. Структура и морфология образцов электродов на основе PbO_2, полученных путем осаждения на поверхность титановой пластины, была исследована с использованием сканирующей электронной микроскопии. Показано, что использование в качестве анода PbO_2 позволяет довести значение ХПК раствора до требуемых норм. После электролиза значения ХПК для всех исследованных концентраций этиленгликоля от 10 до 100 мг/л лежала в пределах 0.34-4.6 мгO_2/л. Изучено влияние плотности тока, концентрации этиленгликоля и хлорида натрия на эффективность электрохимического окисления этиленгликоля.*

***Ключевые слова:** сточные воды, этиленгликоль, аэропорт, окисление, электрохимическая очистка, диоксид свинца.*