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ELECTROCHEMICAL OXIDATION OF PHENOL ON LUMPY ELECTRODES AT A SURGE CURRENT POLARIZATION

Abstract. Phenol which one of the most abundant pollutants in industrial wastewater was investigated for purification. The selected wastewater was provided from the rest of the solution after petroleum producing. This is the major problem for regaining the water without including poisonous contaminants and it should be solved thoroughly. For this purpose lumpy electrodes and a surge current polarization were employed. Phenol oxidation in a stationary mode was carried out by four-sectional electrolyzer which each has 75 mL volume capacity. Anode chambers of purification vessel were equally filled with lumpy electrodes obtained from graphite and they were separated from cathode chambers by porous divisions. Cathode chambers were also completely filled with graphite cores which were used as cathodes. Research of the phenol containing solutions for modeling was selected 10-50 mg/L and sodium sulfate as a background was adjusted with the ratio of 0,25-2,0 g/L. Phenol concentration was defined photometrically. The direct oxidation of phenol on lumpy electrodes at polarization with a surge current has significant advantages when compared to the previous electrochemical methods.

Key words: phenol, electrochemical oxidation, lumpy electrodes, stationary mode, anode, electrochemical method.

Introduction. Phenol which is also called oxybenzene, monohydroxybenzene or phenyl hydroxide has a weak acidity ($K_a=10^{-10}$) and specific fragrance. Phenolic compounds exist in some plants' structure such thyme, carnation and anise. It has been using in multipurpose fields like pesticides, making synthetic resins, perfumes, solvents, pharmaceuticals, dyes, lubricating oils and synthetic tanning agents. It had also used as drug for itching treatments in earlier ages. On the other hand its higher doses have found quite harmful and toxic for the human health in the last decades. Due to the facile solubility in water at room temperature (approximately 9g/100mL) and being miscible with any percentages at more than 65 °C are the main problems for the running water, lakes, seas etc. contaminated by petroleum or any reasons [1-3].

The production of phenol in each year is over 3 million tons so its pollution can't be ignored at all. The human central nervous system, lungs and kidneys are being damaged because of the long-term exposure. Thus, the phenol is classified as a water hazard substance in many countries. The allowed concentration of phenol is only 0.5 mg/L in drinking water. [4]

Purification of wastewater from phenol and its derivatives has carried out by a great number of techniques in particular with chemical oxidation with hydrogen peroxide, ozone [1, 2]. There is a great number of researches devoted to electrochemical oxidation of phenol which cause water contamination for the demand of human being [5-8].

The basic process of purification of water has applied not with direct oxidation of phenol, but also the usage of hydrogen peroxide reagent as it is described as a Fenton's reagent [2, 9-11]. Phenol oxidation has researched on with various modified electrodes by scientists [12-14]. It has been difficult to provide deep cleaning to electrodes in direct oxidation process due to the small contact area with solution that cause decreasing of final installation amount phenol. In the case of application of lumpy electrodes for the purification, it facilitates the handicaps with the aid of using a surge current which essentially reduces the voltage and allows achieving without a rectifier [15]. The lumpy electrodes lead us to remove phenol and

its derivatives from wastewater with an efficient manner. Its structure and purification mechanism have significant and novel properties. The surface of electrodes has been increased and also the recycling of purification process has increased [16-20].

Despite the abundance of investigations on purification of phenol from wastewater, it is really difficult to conclude that the exact procedure has obtained. Because the water structure is unique in each specific case, and deep cleaning requires expensive reagents further recycling operations. So that it shows the all necessity of the further researches of accessible technologies about the purification treatments.

In the present paper, we report the construction of lumpy electrode system which newly used by our research team that provide an effective purification method for phenol from wastewater contaminants. Without requiring additional oxidizing reagents this procedure shows a durable and recyclable aspect.

Materials and Method. Phenol oxidation in a stationary mode was carried out in four-sectional electrolyzer with the each of 75 mL capacity. Anode chambers were equally filled with lumpy electrodes derived from graphite and were split from cathode section by porous partitions. Graphite cores were also completely added into cathode chambers to use as cathode. The construction of lumpy electrode packed system was depicted in Figure 1.

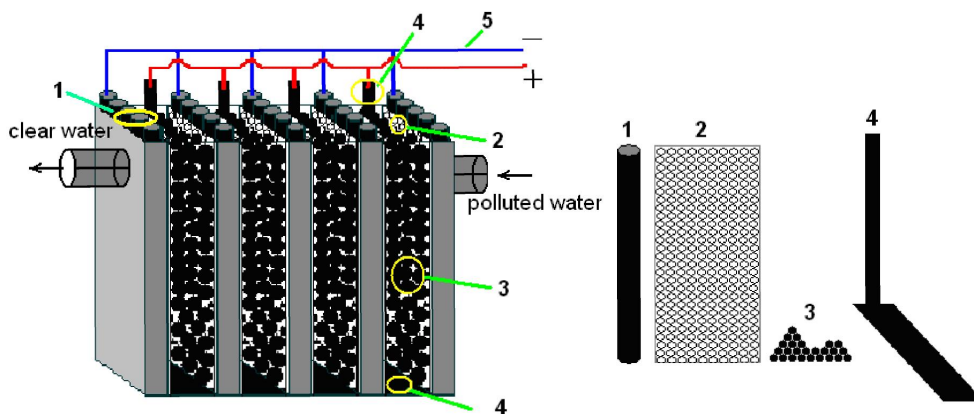


Figure 1 – Construction of lumpy electrode packed system for purification:
 1 – Graphite rods/electrodes, 2 – Plastic walls with apertures, 3 – Lumpy graphite electrodes,
 4 – Current supplier of graphite anode, 5 – Current supplier of cathode (stainless steel)

It is necessary to put free space between cathode and anode electrode chambers for exact cleaning in the given mode. The voltage was moved from an alternating current network through the laboratory auto transformer to adjust current in system. One rectifier diode was also integrated to the system that resulted a creation of the unidirectional pulsing anode current on lumpy electrodes in an anode chambers, and also on electrodes in cathode chambers. Demanded voltage for purification essentially increases when the electrodes connected in parallel type with consecutive connection (Figure 2).

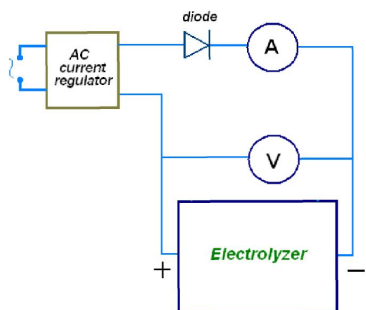


Figure 2 –
 General representation of electrical circuit
 for electrolysis of phenol purification

Phenol containing model solutions for research was prepared between the range of 10-50 mg/L and sodium sulfate was selected about 0,25-2,0 g/L. Phenol concentration was defined photometrically.

Result and Discussion. The influence of current density onto the anodic lumpy electrodes versus the degree of electrochemical destruction of phenol is illustrated in Figure 3. Prior to the current density 115 A/m^2 linear growth of degree of purification is observed. The current strength was 2A, for simplification of calculations the current density was calculated not on the volume area, but on the area of a surface of frontier electrodes.

However at using of lumpy electrodes it is possible to assume that they work as volume electrodes [11].

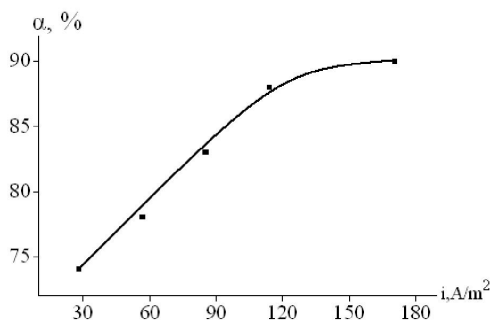


Figure 3 – The purification percentages of phenol at different current densities ($C_{\text{H}}(\text{C}_6\text{H}_5\text{OH}) = 50 \text{ mg/L}$, $\text{Na}_2\text{SO}_4 = 1 \text{ g/L}$, $\tau = 10 \text{ min}$)

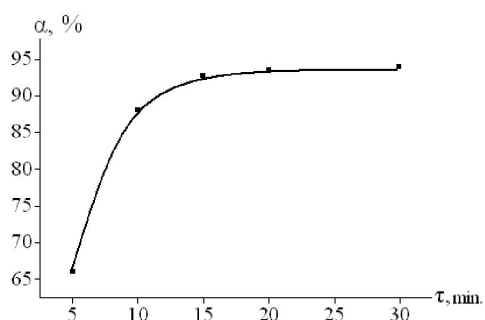


Figure 4 – Degree of purification from phenol from electrolysis duration. ($C_{\text{H}}(\text{C}_6\text{H}_5\text{OH}) = 50 \text{ mg/L}$, $\text{Na}_2\text{SO}_4 = 1 \text{ g/L}$, $i = 115 \text{ A/m}^2$)

As it can be clearly seen in Figure 4, the amount of electrolysis degree of purification practically doesn't change after 15 minutes. The quick reduction of phenol concentration in a solution in first 10 minutes explains that full phenol destruction will be reached after longer time under purification conditions. So after that it will be more practical to clean residual concentration by other methods.

Influence of initial concentration of phenol onto the degree of purification under other constant conditions was investigated. According to Figure 5, as one would expect, increasing the maintenance of phenol in modeling solutions reduces the degree of purification.

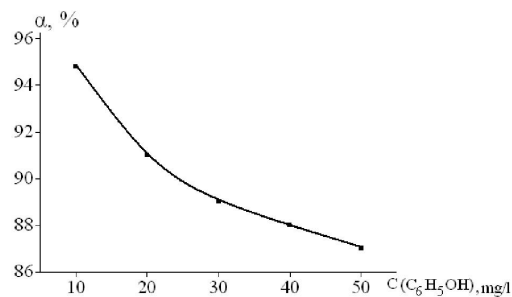


Figure 5 – Degree of purification ability at various initial phenol concentrations ($\tau = 10 \text{ min}$, $\text{Na}_2\text{SO}_4 = 1 \text{ g/L}$, $i = 115 \text{ A/m}^2$)

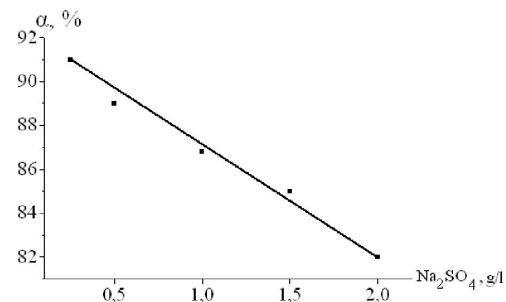


Figure 6 – Degree of purification from phenol at various sodium sulfate concentrations. ($\tau = 15 \text{ min}$, $C_{\text{H}}(\text{C}_6\text{H}_5\text{OH}) = 50 \text{ mg/L}$, $i = 115 \text{ A/m}^2$)

Since sodium sulfate has been chosen as a background, it was necessary to explore the effect of it for this employed process. Background concentration was changed in a range of 0,25-2,0 g/L, and as it is apparently seen from Figure 6, increasing the salt concentration reduces efficiency of process. However, the voltage between anode and cathode electrodes inherently decreases in the case of adding more sodium sulfate salt.

It is also mandatory to control one more important parameter that is known as pH value for purification of wastewater. Because aqueous solutions of phenols have acidic reaction, in particular it is adjusted to 5,5 of pH value for the purification of 50 mg/L phenol concentration. It is obtained that after electrolysis in first 10 minutes pH displaced to 3,3 in the sour medium. The influence of sodium hydroxide concentration in the range of 50-300 mg/L was studied for acidity adjustment. Table 1 shows the pH of the solution after electrolysis in the presence of alkali.

Table 1 – Influence of the sodium hydroxide concentration on the pH after electrolysis

NaOH, mg/L	50	100	150	200	300
pH	5,6	6,3	6,4	6,6	6,8
Note: $\tau=15\text{min}$, $C_{\text{H}}(\text{C}_6\text{H}_5\text{OH})=50\text{ mg/L}$, $i=115\text{ A/m}^2$.					

Thus, as it is shown in Figure 7, there was also a minor alteration for degree of purification, and the process was accompanied by voltage increasing on 0,5 B.

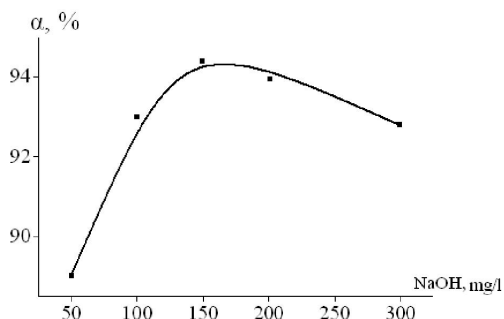


Figure 7 – Degree of purification of phenol from various concentrated sodium hydroxide solutions ($\tau = 15\text{ min}$, $C_{\text{H}}(\text{C}_6\text{H}_5\text{OH}) = 50\text{ mg/L}$, $i = 115\text{ A/m}^2$, $\text{Na}_2\text{SO}_4 = 1\text{g/L}$)

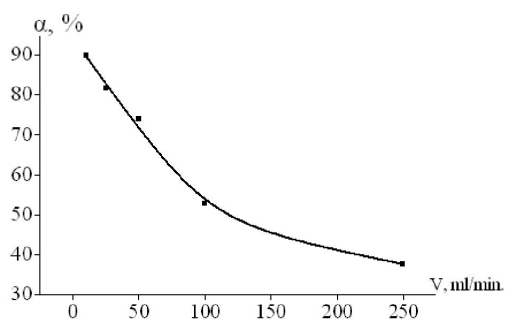


Figure 8 – Degree of phenol purification versus flowing speed ($C_{\text{H}}(\text{C}_6\text{H}_5\text{OH}) = 50\text{ mg/L}$, $i = 115\text{ A/m}^2$, $\text{Na}_2\text{SO}_4 = 1\text{g/L}$)

It was also enlightened that flowing speed of phenol during the purification process in the volume of 1,5 L from 9 sections. By the way, each chamber has also 75 mL volume. In addition electrode chambers were divided by impenetrable partitions to provide electrolyte passing completely through electrolyzer chambers, instead of through them. The amount of the modeling solution passing from was adjusted 1 liter. In appearance, the scale of the removing the phenol from water decreased proportionally (Figure 8).

Also phenol concentration has been measured in various sections of electrolyzer, and apparently from Figure 9, degree of purification grows proportionally to section numbers added.

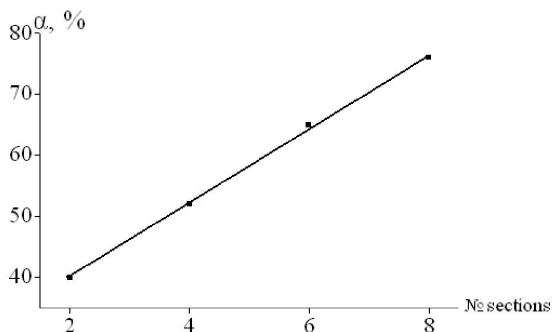


Figure 9 – Degree of purification from phenol in various sections in a flowing mode. ($C_{\text{H}}(\text{C}_6\text{H}_5\text{OH}) = 50\text{ mg/L}$, $i = 115\text{ A/m}^2$, $\text{Na}_2\text{SO}_4 = 1\text{g/L}$)

In table 2, it is summarized the information about influences of some parameters onto the electrolysis conditions such; voltage between electrodes, pHs after electrolysis, temperature change of electrolyte, degree of purification in a stationary mode.

Table 2 – Influence of various parameters for purification after electrolysis

$i, A/m^2$	28	56	84	115	140
$C_{H(C_6H_5OH)} = 50 \text{ mg/L}$, $Na_2SO_4 = 1 \text{ g/L}$, $\tau = 10 \text{ min}$	U=2V pH=5,0 $\Delta t = 2^\circ C$ $\alpha = 74,6\%$	U=3,5V pH=4,4 $\Delta t = 4^\circ C$ $\alpha = 78,3\%$	U=5,5V pH=3,7 $\Delta t = 6^\circ C$ $\alpha = 83,3\%$	U=7,4V pH=3,7 $\Delta t = 7^\circ C$ $\alpha = 88,0\%$	U=10,6V pH=3,5 $\Delta t = 10^\circ C$ $\alpha = 90,0\%$
$\tau, \text{ min}$	5	10	15	20	30
$C_{H(C_6H_5OH)} = 50 \text{ mg/L}$, $Na_2SO_4 = 1 \text{ g/L}$, $i = 115 A/m^2$	U=8V pH=3,5 $\Delta t = 3^\circ C$ $\alpha = 66,1\%$	U=7,4V pH=3,7 $\Delta t = 7^\circ C$ $\alpha = 88,0\%$	U=8V pH=3,6 $\Delta t = 10^\circ C$ $\alpha = 92,8\%$	U=8V pH=3,7 $\Delta t = 16^\circ C$ $\alpha = 93,5\%$	U=8V pH=3,7 $\Delta t = 22^\circ C$ $\alpha = 94,1\%$
$C_{H(C_6H_5OH)}, \text{ mg/L}$	10	20	30	40	50
$\tau = 10 \text{ min}$, $Na_2SO_4 = 1 \text{ g/L}$, $i = 115 A/m^2$	U=8,2V pH=4,8 $\Delta t = 13^\circ C$ $\alpha = 94,8\%$	U=8V pH=3,7 $\Delta t = 12^\circ C$ $\alpha = 91,0\%$	U=7,6V pH=3,6 $\Delta t = 14^\circ C$ $\alpha = 89,3\%$	U=7,3V pH=3,5 $\Delta t = 13^\circ C$ $\alpha = 88,0\%$	U=7,4V pH=3,7 $\Delta t = 7^\circ C$ $\alpha = 88,0\%$
$Na_2SO_4 \text{ g/L}$	0,2	0,5	1,0	1,5	2,0
$\tau = 15 \text{ min}$, $C_{H(C_6H_5OH)} = 50 \text{ mg/L}$, $i = 115 A/m^2$	U=16V pH=3,6 $\Delta t = 24^\circ C$ $\alpha = 91,1\%$	U=12V pH=3,3 $\Delta t = 19^\circ C$ $\alpha = 89,0\%$	U=8,2V pH=3,4 $\Delta t = 13^\circ C$ $\alpha = 86,8\%$	U=6,5V pH=3,4 $\Delta t = 14^\circ C$ $\alpha = 85,8\%$	U=5,7V pH=3,9 $\Delta t = 11^\circ C$ $\alpha = 82,7\%$
$NaOH, \text{ mg/L}$	50	100	150	200	300
$\tau = 15 \text{ min}$, $C_{H(C_6H_5OH)} = 50 \text{ mg/L}$, $i = 115 A/m^2$, $Na_2SO_4 = 1 \text{ g/L}$	U=8,5V pH=5,0 $\Delta t = 13^\circ C$ $\alpha = 89,0\%$	U=8,5V pH=6,3 $\Delta t = 12^\circ C$ $\alpha = 93,6\%$	U=8,4V pH=6,4 $\Delta t = 12^\circ C$ $\alpha = 94,4\%$	U=8,2V pH=6,6 $\Delta t = 13^\circ C$ $\alpha = 93,6\%$	U=7,5V pH=6,8 $\Delta t = 13^\circ C$ $\alpha = 92,8\%$
<i>Note:</i> These results are for a stationary mode.					

Conclusion. Thus, direct oxidation of phenol on lumpy electrodes at polarization by a surge current has following advantages before other electrochemical methods: it is not required additional oxidizing reagents, not spent cheap graphite electrodes are used, isn't required the straightening equipment, probably consecutive connection of several electrolyzers, if necessary.

REFERENCES

- [1] C. Canton, S. Esplugas, J. Casado, Mineralization of phenol in aqueous solution by ozonation using iron or copper salts and light, *Applied Catalysis B: Environmental*, 43 (2003) 139-149.
- [2] S. Esplugas, J. Gimenez, S. Contreras, E. Pascual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, *Water Research*, 36 (2002) 1034-1042.
- [3] H. Shemer, Y.K. Kunkcu, K.G. Linden, Degradation of the pharmaceutical Metronidazole via UV, Fenton and photo-Fenton processes, *Chemosphere*, 63 (2006) 269-276.
- [4] B. Iurascu, I. Siminiceanu, D. Vione, M. Vicente, A. Gil, Phenol degradation in water through a heterogeneous photo-Fenton process catalyzed by Fe-treated laponite, *Water research*, 43 (2009) 1313-1322.
- [5] S. Ahmed, M.G. Rasul, W.N. Martens, R. Brown, M.A. Hashib, Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments, *Desalination*, 261 (2010) 3-18.
- [6] Q. Dai, L. Lei, X. Zhang, Enhanced degradation of organic wastewater containing p-nitrophenol by a novel wet electrocatalytic oxidation process: Parameter optimization and degradation mechanism, *Separation and Purification Technology*, 61 (2008) 123-129.
- [7] U.D. Patel, S. Suresh, Electrochemical treatment of pentachlorophenol in water and pulp bleaching effluent, *Separation and Purification Technology*, 61 (2008) 115-122.
- [8] M.L. Soto, A. Moure, H. Domínguez, J.C. Parajó, Recovery, concentration and purification of phenolic compounds by adsorption: A review, *Journal of Food Engineering*, 105 (2011) 1-27.
- [9] R. Chand, N.H. Ince, P.R. Gogate, D.H. Bremner, Phenol degradation using 20, 300 and 520kHz ultrasonic reactors with hydrogen peroxide, ozone and zero valent metals, *Separation and Purification Technology*, 67 (2009) 103-109.
- [10] V. Kavitha, K. Palanivelu, The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, *Chemosphere*, 55 (2004) 1235-1243.

- [11] V. Kavitha, K. Palanivelu, Degradation of nitrophenols by Fenton and photo-Fenton processes, *Journal of Photochemistry and Photobiology A: Chemistry*, 170 (2005) 83-95.
- [12] S. Andreescu, D. Andreescu, O.A. Sadik, A new electrocatalytic mechanism for the oxidation of phenols at platinum electrodes, *Electrochemistry communications*, 5 (2003) 681-688.
- [13] A. Dabrowski, P. Podkościelny, Z. Hubicki, M. Barczak, Adsorption of phenolic compounds by activated carbon—a critical review, *Chemosphere*, 58 (2005) 1049-1070.
- [14] Y. Wang, K. Chan, X. Li, S. So, Electrochemical degradation of 4-chlorophenol at nickel–antimony doped tin oxide electrode, *Chemosphere*, 65 (2006) 1087-1093.
- [15] J. He, H. Yu, B. Fugetsu, S. Tanaka, L. Sun, Electrochemical removal of bisphenol A using a CNT-covered polyester yarn electrode, *Separation and Purification Technology*, 110 (2013) 81-85.
- [16] C. Belaid, M. Khadraoui, S. Mseddi, M. Kallel, B. Elleuch, J.F. Fauvarque, Electrochemical treatment of olive mill wastewater: Treatment extent and effluent phenolic compounds monitoring using some uncommon analytical tools, *Journal of Environmental Sciences*, 25 (2013) 220-230.
- [17] R. Berenguer, J.P. Marco-Lozar, C. Quijada, D. Cazorla-Amorós, E. Morallón, Electrochemical regeneration and porosity recovery of phenol-saturated granular activated carbon in an alkaline medium, *Carbon*, 48 (2010) 2734-2745.
- [18] Y.-h. Cui, X.-y. Li, G. Chen, Electrochemical degradation of bisphenol A on different anodes, *Water research*, 43 (2009) 1968-1976.
- [19] G. Gao, C.D. Vecitis, Electrocatalysis aqueous phenol with carbon nanotubes networks as anodes: Electrodes passivation and regeneration and prevention, *Electrochimica Acta*, 98 (2013) 131-138.
- [20] H. Ma, X. Zhang, Q. Ma, B. Wang, Electrochemical catalytic treatment of phenol wastewater, *Journal of Hazardous Materials*, 165 (2009) 475-480.

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ИМПУЛЬСТІ ТОКПЕН ПОЛЯРИЗАЦИЯЛАНҒАН ФЕНОЛДЫҢ ТҮЙІРШІКТІ ЭЛЕКТРОДТАРДА ЭЛЕКТРОХИМИЯЛЫҚ ТОТЫҒУЫ

Аннотация. Өндірістік ағызынды суларда кеңінен таралған фенолдан тазалау процесі зерттелді. Мұнай бөліп алынғаннан соң қалған ерітінді зерттеу үшін ағызынды су ретінде қолданылды. Бұл ағызынды суда зиянды ластағыштар болғаны себепті он қайта қолдану барысында бір қатар қиындықтар туады, сол себепті бұл мәселе шешуді талап етеді. Бұл мәселені шешу үшін біз түйіршікті электродтарды қолдана отырып импульсті токпен поляризациялау әдісін қолдандық. Фенолдың тотығу стационарлы режимде, әр секцияның көлемі 75 мл болған төрт секциялы электролизерде жүргіздік. Анодты камералар графиттан тұратын түйіршікті электродтармен толтырылып, катодты камералардан кеуекті бөліктермен ажыратылған. Ал катодты камералар катод қызметін атқаратын графит таяқшаларымен толтырылды. Құрамында фенол бар ерітіндіні зерттеу мақсатында модельдеу үшін 10-50 мг/л натрий сульфаты фон ретінде алынып, 0,25-2,0 г/л-ге дейін келтіріліп отырды. Фенол концентрациясы фотометриялық әдіспен анықталды. Импульсті токпен поляризациялай отырып түйіршікті электродтар қатысында фенолдың тура тотығу әдісі бұдан алдыңғы электрохимиялық әдістермен салыстырғанда анағұрлым артықшылықтары бар.

Түйін сөздер: фенол, электрохимиялық тотығу, түйіршікті электродтар, стационарлы режим, анод, электрохимиялық әдіс.

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ЭЛЕКТРОХИМИЧЕСКОЕ ОКИСЛЕНИЕ ФЕНОЛА НА КУСКОВЫХ ЭЛЕКТРОДАХ ПРИ ПОЛЯРИЗАЦИИ ИМПУЛЬСНЫМ ТОКОМ

Аннотация. Исследован процесс очистки от фенола, являющегося одним из самых распространенных загрязняющих веществ в промышленных сточных водах. Отобранные сточные воды были получены из оставшейся части раствора после добычи нефти. Это является основной проблемой для повторного использования воды, так как она содержит ядовитые загрязнения, и это требует срочного решения. Для решения этой проблемы нами использовались кусковые электроды и поляризация импульсным током. Окисление фенола в стационарном режиме проводили с помощью четырехсекционного электролизера, каждый из которых имел емкость объемом 75 мл. Анодные камеры были одинаково заполнены кусковыми электродами, полученными из графита, и они были отделены от катодных камер пористыми делениями. Катодные камеры также были полностью заполнены графитовыми стержнями, которые использовались в качестве катодов. Для исследования фенолосодержащих растворов для моделирования было выбрано 10-50 мг/л сульфата натрия в качестве фона, и было отрегулировано в соотношении 0,25-2,0 г/л. Концентрацию фенола определяли фотометрически. Прямое окисление фенола на кусковых электродах при поляризации импульсным током имеет значительные преимущества по сравнению с предыдущими электрохимическими методами.

Ключевые слова: фенол, электрохимическое окисление, кусковые электроды, стационарный режим, анод, электрохимический метод.