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APPLICATION OF ELECTROCHEMICALLY SYNTHESIZED FERRATE (VI) IN THE TREATMENT OF PHENOL CONTAMINATED WASTEWATER FROM WOOD INDUSTRY

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Abstract: Treatment of wastewater (WW) from wood industry is of great importance due to high concentration and toxicity of phenol and its derivatives. High concentration of phenol in WW of wood industry originates from pentachlorophenol (PCP), which is used for wood conservation. According to the Regulations on Hazardous Substances in Water [1] allowed phenol concentration in waters of the III and IV class is 300 mg/l. Conventional methods for removal of phenol from WW are either environmentally or economically unacceptable. The use of ferrate (VI) as a multifunctional chemical reagent has significant advantages over conventional methods. The subject of this paper is treatment of samples of WW from wood industry - from thermal dryer and steam chamber, by electrochemically synthesized ferrate (VI). The initial concentration of phenol in the sample from thermal dryer was 27 mg/l and in the sample from steam chamber 30 mg/l. This wastewater also has a high content of natural organic matter (COD of the sample from the thermal dryer was 3233.1 mgO_2/l and COD of the sample from the steam chamber was 4692.1 mgO_2/l). The efficiency of phenol removal by ferrate (VI) was 74.85% and 72.67% for samples from thermal dryer and steam chamber, respectively.

Keywords: ferrate (VI), phenol, wood industry, wastewater treatment, COD

INTRODUCTION

A large amount of attention has recently been focused on the removal of phenol and its derivatives from wastewater (WW) due to their toxicity and high concentration in wastewater. Phenol is a common pollutant in industrial discharges and is also believed to be an intermediate product in the oxidation process of higher molecular weight aromatic hydrocarbons. Their high concentration in the WW of wood industry originates from pentachlorophenol (PCP), which is used for wood conservation [2].

The contamination of water system by phenols and their compounds is a major problem because of the toxicity of phenol even at low concentrations. Toxic phenol concentrations are in the range of 10 - 24 mg/l for humans and from 9 - 25 mg/l for aquatic life. Lethal concentration of phenol is around 150mg/100ml [3]. Phenol and phenolic compounds are designated as priority pollutants by the Environmental Protection Agency in the US, and take 11th place in the list of 126 undesirable chemicals [4].

Phenol and phenolic compounds are classified as teratogenic and carcinogenic compounds [5]. Phenolic compounds are well known for high salinity, acidity, chemical oxygen demand (COD) and low biodegradability [6]. In addition, they have low volatilities and easily form azeotropes and eutectics [7]. All these properties make them difficult to treat.

Phenol has acute and chronic effects on human health [4]. Inhalation and dermal exposure to phenol is highly irritating to skin, eyes, and mucous. The other acute health effects are headache, dizziness, fatigue, fainting, weakness, nausea, vomiting and lack of appetite at high levels. Effects from chronic exposure (longer than 365 days) include irritation of the gastrointestinal tract. Phenol also can change blood pressure and can cause liver and kidney damage. Nervous system is affected negatively for long time exposures. Animal studies have not shown tumors resulting from oral exposure to phenol, while dermal studies have reported that phenol applied to the skin may be a tumor promoter and/or a weak skin carcinogen in mice.

Due to its toxicity to aquatic life and humans, regulations for phenol concentration in WW are very strict. Maximum allowable discharge concentration of phenol varies from country to country, but generally it is about 10 mg/l [8]. According to the Ordinance on Hazardous Substances in Water [1] the maximum content of phenol in the waters of categories I and II is 1 mg/l, while in the waters of categories III and IV the limit is 300 mg/l.

Conventional methods for removing phenolics from wood industry WW include biological degradation, solvent extraction, adsorption and chemical oxidation [6, 9–11].

Biological treatment is economical and environmentally friendly method but at high concentrations of phenol, application of this method is not possible because of the inactivation of microorganisms. Other disadvantages are necessity of large land area and long time for microbial degradation, which makes this process less flexible in design and operation [12].

In the solvent extraction method the residual phenol concentration in wastewater barely meets the strict US Environmental Protection Agency (EPA) requirements (less than 1 mg/L in the wastewater) [13]. What is more, the separation of solute from the solvent is expensive and the loss of solvent requires additional treatment.

The adsorption process is proven to be efficient for the removal of organic contaminants and it is usually used only to treat dilute wastewater [14]. The most popular adsorbent is activated carbon due to its excellent adsorption abilities for phenolic compounds [15]. Drawback of this method is high initial cost; the regeneration of saturated carbons is also costly and results in loss of adsorbents. In addition, this treatment requires complexing agents to improve properties of activated carbon [15].

One of the possible methods of phenol removal from aqueous environments is chemical oxidation by ferrate (VI), an environmentally friendly oxidant, coagulant and disinfectant (Jiang, 2007). Ferrate(VI) is an adequate alternative to conventional methods because of its suitable physical and chemical properties such as high oxidation potential (2.2 V in acidic conditions and 0.7 V in alkaline conditions), forming of oxygen from water oxidation and high capacity for coagulation of iron(III)hydroxide as a product of ferrate(VI) reduction [16]. Ferrate (VI) can be produced by chemical or electrochemical synthesis. Ferrate (VI) produced by electrochemical synthesis has many advantages compared to chemically synthesized ferrate (VI) [17], such as simplicity and cost-effectiveness of the treatment (the use of one chemical, one system for dosing an mixing and less sludge production), exceptional purity of obtained ferrate (VI), as well as avoiding the formation of toxic by-products which originate from the application of chlorine and its compounds. Chlorine-based oxidants are not favorable option due to reaction of phenol with dissolved organic compounds and formation of toxic chlorine organic compounds such as 2-chlorphenol [18]. One more advantage of electrochemically produced ferrate (VI) is that it has no instability problem and needs no transportation, and because of ecological advantages it can be implemented in wastewater treatment practice, *in situ*.

The aim of this paper is to examine the possibility of phenol removal from wood industry WW by electrochemically synthesized ferrate (VI).

MATERIAL AND METHODS

Two wastewater samples from the wood processing plant were used in the experimental work: a sample from the thermal dryer and a sample from the steam chamber. The initial concentration of phenol in the sample from the thermal dryer was 27 mg/l and in a sample from the steam chamber 30 mg/l. This wastewater is also characterized by a high content of natural organic matter. Chemical oxygen demand (COD) of the sample from the thermal dryer was 3233.1 mg O_2/l and of the sample from the steam chamber 4692.1 mg O2/l. pH value of the sample from the thermal dryer was 4 and pH value of the sample from the steam chamber was 5.

The process of the treatment was performed using Jar test with a four-unit stirrer (Velp JLT4).

In the first step of the treatment both samples were treated with 30 mg/l $KAl(SO_4)_2$ of p.a. quality purchased at Sigma-Aldrich, St. Louis, Missouri, USA in order to remove suspended solids with a prior setting of pH value to 7.

Figure 1. Device for electrochemical synthesis of ferrate (VI)

In the second step of the treatment the samples were treated with the solution of electrochemically synthesized ferrate (VI) concentration of 8 g/l in molar ratio phenol: ferrate (VI) = 1 : 5. The process of electrochemical synthesis of the alkaline solution of ferrate(VI) was based on transpassive anodic dissolution of iron alloys in a 10 M NaOH solution, in accordance with previous studies [17,19] and it was carried out in a laboratory facility for electrochemical synthesis of ferrate (VI), Fig. 1.

The change in the concentration of phenol and COD value of the samples were determined using standard methods at MOL Institute, Stara Pazova.

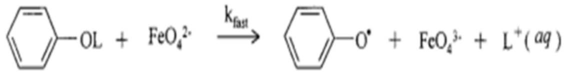
RESULTS AND DISCUSSION

Results of phenol removal by ferrate (VI) from the samples of wastewater from the thermal dryer and steam chamber are shown in Table 1.

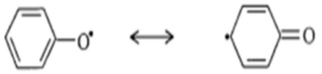
Table 1. Reduction of the phenol concentration in the samples of wastewater from the thermal dryer and steam chamber before and after the treatment

	Phenol concentration in the untreated sample, mg/l	Phenol concentration in the treated sample, mg/l	Removal efficiency, %
Thermal dryer	27	6,79	74,9
Steam chamber	30	8,20	72,7

The results of the treatment shows high removal efficiency of phenol by ferrate (VI), 74.9% and 72.7%, for wastewater from thermal dryer and steam chamber, respectively, Table 1. Phenol is removed from aqueous solution by flocculation and coagulation with ferrous hydroxide, reactions 1–3, which is obtained as a product of ferrate (VI) reduction and has a very developed absorption area [20]. Since ferrous hydroxide has an extremely low solubility in these conditions, presence of residual Fe is not expected.



(1)



(2)

(3)

Possibility of phenol removal using ferrate (VI) was additionally confirmed by determining the value of COD in the samples treated by ferrate (VI), Table 2.

Table 2. Percentage of COD removal during oxidation reaction of phenol by ferrate (VI)

	COD of untreated sample, mgO$_2$/l	COD of treated sample, mgO$_2$/l	Reduction efficiency of COD, %
Thermal dryer	3233.1	2384	26.3
Steam chamber	4692.1	2594	44.7

The samples from thermal dryer, Figure 2, and steam chamber, Figure 3, were also characterized by high initial COD values, 3233.1 and 4692.1 mgO$_2$/l, for thermal dryer WW and steam chamber WW, respectively.

(a) (b) (c)

Figure 2. Sample of WW from the thermal dryer (a) before the treatment; (b) after the first step of the treatment by KAl(SO$_4$)$_2$; (c) after the second step of the treatment by ferrate (VI)

After the addition of ferrate (VI) into the solution, showed a COD reduction of 26.3 % for thermal dryer and 44.7 % for steam chamber. Using higher doses of ferrate (VI) could reach a more efficient reduction of COD values which requires further optimization of the treatment process of WW from wood industry by ferrate (VI).

Figure 3. Sample of WW from the steam chamber before the treatment and after the second step of the treatment by ferrate (VI)

CONCLUSIONS

The aim of this study was to examine the possibilities of phenol removal from WW from wood industry in the reaction of oxidation by freshly electrochemically synthesized ferrate (VI).

The paper shows the possibility of efficient removal of phenol by ferrate (VI) from the samples of wastewater from wood processing industry characterized by a high content of phenols and high COD value. Due to the catalytic effect of ferrous hydroxide, resulting product from the reaction of ferrate (VI) reduction, high efficiency of phenol removal from the wastewater is achieved: 74.9 % removal efficiency for the sample from thermal dryer and 72.7% removal efficiency for the sample from steam chamber. Since the treated water had a high COD value for more effective treatment it is necessary to increase the added amount of ferrate (VI).

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REFERENCES

[1.] Regulation on hazardous substances in water, Official Gazette of SRS, no. 31/82

[2.] Lee L., Rao P., Brusseau M., Nonequilibrium sorption and transport of neutral and ionized chlorophenols, Environmental Science & Technology, Vol.25, pp. 722-729, 1991

[3.] Kulkarni S., Kaware J., Review on Research for Removal of Phenol from Wastewater, International Journal of Scientific and Research Publications, Vol. 3, pp. 1-4, 2013

[4.] Manual Report for List of Chemical Priority, Environmental Protection Agency (EPA), USA, 2002

[5.] Iurascu B., Siminiceanu I., Vione D., Vicente M.A., Gil A., Phenol degradation in water through a heterogeneous photo-Fenton process catalyzed by Fe treated laponite, Water Research, Vol. 43, pp. 1313–1322, 2009

[6.] Turhan K., Uzman S., Removal of phenol from water using ozone, Desalination, Vol. 229, pp. 257–263, 2008

[7.] López-Montilla J., Pandey S., Shah D., Crisalle O., Removal of non-ionic organic pollutants from water via liquid-liquid extraction, Water Research, Vol. 39, pp. 1907–1913, 2005

[8.] Yamada K., Akiba Y., Shibuya T., Kashiwada A., Matsuda K., Hirata M., Water purification through bioconversion of phenol compounds by tyrosinase and chemical adsorption by chitosan beads, Biotechnology Progress, Vol. 21, pp. 823-829, 2005

[9.] Nair C. I., Jayachandran K., Shashidhar S., Biodegradation of phenol, African Journal of Biotechnology, Vol. 25, pp. 4951–4958, 2008

[10.] Jiang H., Fang Y., Guo Q. X., Studies on the extraction of phenol in wastewater, Journal of Hazardous Materials B, Vol. 101, pp. 179–190, 2003

[11.] Hameed B. H., Rahman A. A., Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material., Journal of Hazardous Materials, Vol. 160, 576–581, 2008

[12.] Kibret M., Somitsch W., Robra K. H., Characterization of phenol degrading mixed population by enzyme assy, Water Research, Vol. 34, 1127–1134, 2000

[13.] Pinto R. T. P., Lintomen L., Luz L. F. L., Wolf-Maciel, M. R., Strategies for recovering phenol from wastewater: Thermodynamic evaluation and environmental concerns, Fluid Phase Equilibria, Vol. 228-229, pp. 447–457, 2005

[14.] Rengaraj S., Moon S. H., Sivabalan R., Arabindoo B., Murugesan V., Removal of phenol from aqueous solution and resin manufacturing industry wastewater using an agricultural waste: Rubber seed coat. Journal of Hazardous Material, Vol. 89 pp. 185–196, 2002

[15.] Ahmaruzzaman M., Adsorption of phenolic compounds on low-cost adsorbents: A review, Advance in Colloid and Interface Science, Vol. 143, p. 48□67, 2008

[16.] Sharma V. K., Potassium ferrate(VI): an environmentally friendly oxidant, Advances in Environmental Research, Vol. 6, pp. 143-156, 2002

[17.] Nikolić-Bujanović Lj., Simičić M., Čekerevac M., Electrochemical preparation of solid ferrates(VI), Hemijska Industrija, Vol. 66, pp. 455–460, 2012

[18.] Waite T., Gilbert M., Oxidative destruction of phenol and other organic water residuals by iron (VI) ferrate, Water Pollution Control Federation, Vol. 50, pp. 543-551, 1978

[19.] Čekerevac M. I., Nikolić-Bujanović Lj. N., Mirković M. B., Popović N. H., Application of electrochemically synthesized ferrate(VI) in the purification of wastewater from coal separation plant, Hemijska Industrija, 64, pp. 423-430, 2010

[20.] Jiang J.-Q., Lloyd B., Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment, Water Research, Vol. 36, pp. 1397-1408, 2002

[21.] M. Tomić, L. Nikolić Bujanović, M. Čekerevac, M. Zdravković, M. Stamenković Đoković, Application of electrochemically synthesized ferrate (VI) in the treatment of phenol contaminated wastewater from wood industry, The VIth International Conference Industrial Engineering and Environmental Protection 2016 – IIZS 2016

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