Manažérstvo životného prostredia 2013 ♦ Management of Environment´2013
Zborník z XIII. medzinárodnej vedeckej konferencie, 18. - 19. apríl 2013, Bratislava
Proceedings of the 13rd International Conference, Bratislava, April 18-19, 2013
■ Žilina: Strix. Edícia ESE-14, 1. vyd., ISBN 978-80-89281-90-9 ■ Rusko, M. [Ed.] ■

USING OF AOP PROCESS FOR PHENOL REMOVAL FROM WASTEWATER

Blanka GALBIČKOVÁ - Maroš SOLDÁN

ABSTRACT: *Advanced oxidation processes (AOPs) have been developed as an alternative technology for hazardous organic treatment in industrial wastewater. For phenol removing from wastewater traditional disinfection by chlorine is not appropriate because of generating more toxic pollutants - chlorophenols so AOPs are widely used for disinfection of this kind of pollutants. In this paper for phenol degradation is used physico-chemical method (ozonization). Also influence of catalyst is monitored. As catalyst red mud and black nickel mud are used. These catalysts are waste from metal production. Results from analyses are compared.*
Keywords: *phenol, ozonization, red mud, black nickel mud, MS-GC*

VYUŽITIE AOP PROCESU NA ODSTRÁNENIE FENOLU Z ODPADOVEJ VODY

ABSTRAKT: *Pokročilé oxidačné procey (AOP)sa v súčasnosti využívajú ako alternatívny spôsob odstraňovania nebezpečných polutantov z piemyselných odpadových vôd. V prípade odstraňovania fenolu z odpadových vôd nieje tradičná dezinfekcia vôd veľmi vhodným spôsobom, nakoľko vznikajú chlórfenoly, ktoore sú toxickejšie ako samotný fenol. AOP majú v pípade takýchto polutantov široké využitie. V článku je na degradáciu fenolu použitá fyzikálno-chemická metóda (ozonizácia) a taktiež je sledovaný vplyv katalyzátorov na tento process. Ako katalyzátory sa používajú červený kal a lúženec, ktoré sú odpadmi z výroby kovov. V závere sú porovnané výsledky odsttraňovania fenolu s použitím katalyzátorov a bez nich.*
Kľúčové slová: fenol, ozonizácia, červený kal, lúženec

INTRODUCTION

Phenols are pollutants of high priority concerns because of their toxicity and possible accumulation in the environment. Phenols are introduced into surface water from industrial effluents such as those from the coal tar, gasoline, plastic, rubber proofing, disinfectant, pharmaceutical and steel industries and domestic wastewaters, agricultural run-off and chemical spills. [1] On the base of toxicity and carcinogenicity of some phenol compounds according to US EPA phenol was proposed to position of 11 from 129 priority monitored chemical compounds in the environment [2]. According to IARC phenol is not proven carcinogen to animal or human. It is classified as mutagen of class 3 and it is proven as a genetic toxicant for animal (mouse, rat) [3].

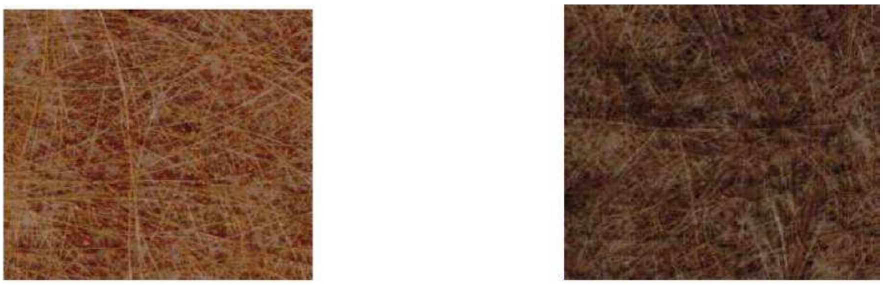
AOPs have lately shown promise for water and wastewater treatment. The primary oxidant responsible for the oxidation of organic compounds is the highly reactive hydroxyl radical. Many different techniques can be employed to generate hydroxyl radicals with all methods involving the use of an oxidant together with an activating system. Ozonization is very effective in treating wastewaters containing phenolic compounds. Ozone reacts with aqueous compounds in two ways: direct reactions of the molecular ozone with the compounds, and indirect reactions of the radicals resulting from the decomposition of ozone with radical reactions are non-selective and fast. Furthermore, the decomposition of ozone is catalyzed by OH- ions, and proceeds more rapidly with increasing pH [4]. Many research efforts have been devoted to develop methods for eliminating of phenolic compounds from soil and water by means of biological and physico-chemical methods [5].

Red mud residues as unconventional adsorbents for water and wastewater treatment are motivated by the fact that red mud is a fine-grained mixture of oxides and hydroxides, capable of removing several contaminants, as well as being widely available [1]. Red mud is a waste from production of Al_2O_3. The most common for Al_2O_3 is Bayer process. Red mud contains Fe_2O_3 (31.80 wt. %), TiO_2 (22.60 wt. %), Al_2O_3 (20.10 wt. %), SiO_2 (6.10 wt. %), CaO (4.78 wt. %), Na_2O (4.70 wt. %), MgO (0.20 wt. %), K_2O (0.03 wt. %) [6]. In Slovakia red mud was produced by aluminium plant in Žiar nad Hronom.

The result of nickel and cobalt production is huge amount of black nickel mud. For nickel production hydrometallurgical processes are used. Black nickel mud contains Fe_2O_3 (38.50 wt. %), FeO (25.63 wt. %), SiO_2 (17.57 wt. %), Al_2O_3 (4.99 wt. %), Cr_2O_3 (3.31 wt. %), Mo (3.19 wt. %), CaO (3.20 wt. %), MnO (0.52 wt. %), C (0.50 wt. %), Ni (0.24 wt. %), Na_2O (0.23 wt. %), TiO_2 (0.17 wt. %) and others (< 0.01 wt. %) [7]. Danger point of view is polymetallic dust which spreads into the environment. Despite the high value of oxides of iron (95 %) black nickel mud can not be used for iron production because of a great content of chromium (approx. 3 %) [8]. Neutralized black nickel mud has (as red mud) large specific surface area and is widely use as an adsorbent and coagulant in the remediation of waters in agriculture and also in the technology of wastewater cleaning and in chemical industry. The plant for this production was situated in Sereď.

Experiment

In this paper AOP is used for phenol removal from prepared 100 ml of aqueous solution with concentration 10^{-3} mol.dm^{-3}. We followed the impact of (1) time ozonization (60 min. and 180 min.) and (2) presence of catalyst to degradation of phenol from solution. Experiments were performed by room temperature. For ozonization was used ozone generator Sander S500 with ozone flux 400 cm of gas per minute. Catalyst red mud and black nickel mud we used for improve of degradation of phenol from aqueous solution. Catalysts (1g) are fixed on glass wool surface in the area 20 x 20cm (Fig. 1). On glass wool adssorbent is covered and it is annealed in muffle furnace in order to reach the best available value for foxation of adsorbent, for removing possible organic contamination of adsorbent and by heat the particle of adsorbent are crushed into finer so it also increase adsorption capacity of adsorbent. The same amounts of both nickel and red mud were added to the system.



a) Red mud b) Black nickel mud

Fig.1 Catalyst annealed on the glass wool surface

Concentration of phenol was monitored by gas chromatography- mass spectroscopy (GC- MS). GC-MS was carried out using an Agilent 5975C Gas Chromatograph equipped with a capillary column (30 m x 0.250 mm internal diameter) with film 0.25 µm and a He mobile phase.

Abundance of detector in phenol sample prepared (with concentration of phenol 10^{-3} mol.dm^{-3}.) is 1.443.141. Efficiency of phenol removal is calculated by Eq. 1, where A_0 is abundance of detector in phenol sample prepared (t_0) and A_t is abundance of phenol sample in time 60/180 min. (after ozonization).

$$\eta_t = \frac{A0 - At}{A0} . 100\ [\%]$$

Results

In the next figures are shown results from experiments. In the Fig. 2 are shown results from degradation of phenol by ozonization (60 min.) without and with catalysts (red mud and black nickel mud). As we can see approximately 95 % of phenol was removed from solution by ozonization without catalyst. Approximately 42 % was removed by ozonization with catalyst black nickel mud. Approximately 51 % of phenol was removed by ozonization with red mud as catalyst. More of phenol was removed only with ozonization without catalyst.

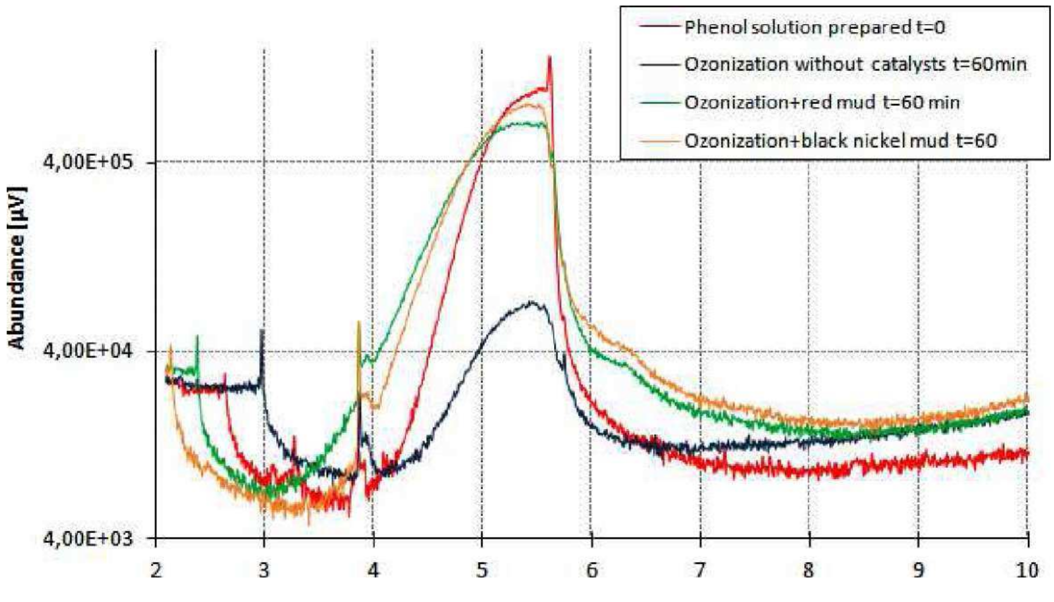


Fig.2 Chromatogram of phenol solution after ozonization (60 min.)

In the Fig.3 are shown results from degradation of phenol by ozonization (180 min.) without and with catalysts. As we can see approximately 99 % of phenol was removed from solution by ozonization without catalyst. Approximately 45 % was removed by ozonization with catalyst black nickel mud. Approximately 54 % of phenol was removed by ozonization with red mud as catalyst. Less of phenol was removed with ozonization with catalysts as without catalysts.

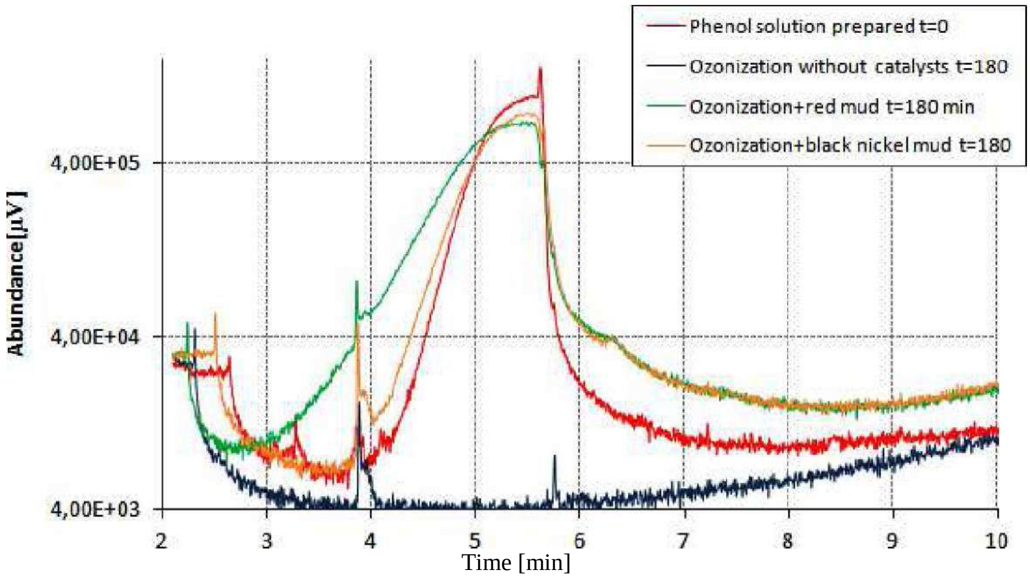


Fig.3 Chromatogram of phenol solution after ozonization (180 min.)

SUMMARY

AOP processes are used for wastewater treatment. It's used for oxidation of organic compounds from water solution. On the basis of the results obtained we can confirm oxidisability of ozone. Percentages of remove phenol are increases with increasing time of ozonization. Catalyst red mud and black nickel mud we used for improve of degradation of phenol from aqueous solution. These catalysts caused that more phenol was removed by ozonization without catalysts as with ozonization with catalyst.

Acknowledgements

This contribution was created with the support of the Operational Programme Research and Development for project: *„Hybridpower source for technical and consulting laboratory use and promotion of renewable energy sources'"* (ITMS 26220220056), financed from resources of the European Regional Development Fund and Promoting young researchers 2013 (Slovak University of Technology in Bratislava)

REFERENCES

[1] Su-Hsia Lin, Ruey-Shin Juang. Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review. In *Journal of Environmental Management.* Vol. 90 (2009) p. 1336-1349

[2] A. TOR et al. Removal of phenol from aqueous phase by using neutralized red mud. In *Journal of Colloid and Interface Science.* Vol. 300 (2006) p. 498-50

[3] Materials and safety data sheet. Phenol [online] <www.slovnaft.sk/repository/539132.pdf>

[4] M. Soldan, M. Sirotiak, A.. MichaHkova. Catalytic ozonization of phenol with the use of alternative catalysts. In *Advanced Materials Research.* Vols. 781-784 (2013)

[5] A. Barrera et al. Reusable PdO/Al_2O_3-Nd_2O3 photocatalysts in the UV photodegradation of phenol. In *Applied Catalysis B: Environmental.* Vol. 144 (2014) p. 362-368

[6] Z. Soldanova, M. Soldan. Use of adsorptive properties of wastes from the production of metals [online] <http://www.mtf.stuba.sk/docs//internetovy_casopis/2005/2/soldan%202.pdf>

[7] M. Soldan, M. Chelebcokova. Catalytic ozonization of phenol with the use of black nickel mud. In *MtF STU*.[online] <http://www.mtfstuba.sk/docs//internetovy_casopis/2005/2/soldan%201.pdf>

[8] Ground Water Recharge Using Waters of Inpaired Quality; National Research Council, National Academy Press; Washinghton, D C , 1994, 55 p., ISBN: 0-309-05142-8

AUTHOR'S ADDRESSES:

Blanka GALBIČKOVÁ, Ing, Faculty of Materials Science and Technology, Slovak University of Technology, Botanická 49, 91701 Trnava, Slovak Republic, e-mail: blanka.galbickova@stuba.sk

Maroš SOLDÁN, prof, Faculty of Materials Science and Technology, Slovak University of Technology, Botanická 49, 91701 Trnava, Slovak Republic, e-mail: maros.soldan@stuba.sk

REVIEWER:

Ružena KRÁLIKOVÁ, Assoc. prof., Ing., PhD., Technical University in Košice, Park Komenského 5, 04001 Košice, Slovakia, e-mail: ruzena.kralikova@tuke.sk