Koc. J. Sci. Eng., 1(2): (2018) 42-45

Kocaeli University



Kocaeli Journal of Science and Engineering (KOJOSE)



#### http://dergipark.gov.tr/kojose

# Degradation of 2-Chlorophenol Present in Effluent Water by Advanced Electrochemical Method

M. Saeed ULLAH<sup>1,\*</sup>, Aziz Ur Rehman MAJID<sup>1</sup>, Umair ZAHID<sup>2</sup>, Ghulam ABBAS<sup>3</sup>, Yusra SHAHID<sup>2</sup>, Ayesha MAROOF<sup>5</sup>

<sup>1</sup>Department of Chemical Engineering, Kocaeli University, Kocaeli, 41310, Turkey

<sup>2</sup>University of the Punjab, 54000, Lahore, Pakistan

<sup>3</sup>Department of Chemical Engineering, University of the Gujarat, 50700, Gujarat, Pakistan

<sup>4</sup>Istanbul Ticaret University, Küçükyalı, 34840, İstanbul, Turkey

Article Info	Abstract
Research paper	Water is an important of life. When it is polluted, it disturbs not only human but also aquatic life. There are no of chemicals that contaminate the water. Industries generate different types of chemicals,
Received : 17/04/2018 Accepted : 24/10/2018	which pollute the water. Effluent from these industries contains heavy metals, BOD, COD and phenolic compounds. Water pollution is a very serious issue. Different ways are available to treat the waste water. Flocculation, sedimentation, coagulation, photolysis and electrochemical methods are used for treatment of waste water. Phenolic compounds are the most harmful chemicals present as contamination in waste water. Phenolic compound accompanied with chlorine can exist as mono-
Keywords	chlorophenol, di-chlorophenol and tri-chlorophenol. These compounds are very carcinogenic in nature
Electrochemical Treatment Electrodes Harmful Chemicals Phenolic Degradation Treating Time Voltages	so their presence is dangerous for human as well as aquatic life. In this research electrochemical method is used to treat <i>o</i> -chlorophenol. Effect of electrodes, voltages and treating times on the removal efficiency have been studied. Stander sample of 100ppm from stock material have been prepared as an analogues to the waste water of industries. HPLC/UV detector is used to analyze the treatment effects. Graphite electrode, 20 volts and 20 min operating time is the most effective parameters that removes about 60% of the initial concentration of 2-CP (ortho-chlorophenol).

# 1. Introduction

Water is a transparent, tasteless, odorless, and nearly colorless chemical substance that is the main constituent of Earth's streams, lakes, and oceans, and the fluids of most living organisms. It is usually polluted due to different industrial activities done by human beings [1]. For drinking purpose, water should be clean and free from contamination. It is the first and fundamental right of human beings and other organisms. For this purpose, we should not only install some technological equipment for the reuse of water, but also have to save our natural resources from contaminations. To make these efforts fruitful and serious collective efforts are being done all around the world. Basically if we treat our waste from pollutants which have been adverse effects on the naturally available water resources, we will be able to save our natural resources of water as well as aquatic lives [2]. It is necessary to eliminate or treat different contaminants present in wastewater before drainage. Numbers of ways are available to treat the waste water. Flocculation, sedimentation, coagulation, photolysis, advance oxidation, ozonation and electrochemical methods are used for treatment of wastewater [3-7].

Phenolic compounds are the most harmful chemicals present as contamination in wastewater. Phenolic compounds consist of mono-chlorophenol, di-chlorophenol and tri-chlorophenol. These compounds are very toxic and their presence is dangerous for human as well as aquatic life. These compounds are found in the wastewater of textile[8], pharmaceutical, petrochemicals, pesticides and synthetic fiber industries [9]. Environmental Protection Agency (EPA) has given the standards for the wastewater. To reduce the quantities of phenolic compounds

Corresponding Author: engrsaeed147@gmail.com

in the exhausted water a number of treatments are available [8,10].

In Pakistan, most common method to treat the toxic compounds is the biological method [11]. In which microbial activities have been done to decompose or degrade the toxic organic components of the wastewater [12]. In this scenario the activity of biological sludge is the most important, which is usually decreased due to the varying concentrations of phenolic compounds. As well as it is due to the toxic in nature, sometimes these methods seem inefficient. Secondly, the biological treatment requires a type of pond and due to high rates of commercial land, this procedure feels to be high initial cost. Other drawback of this method is the disposal of bio sludge [13].

Other method is the chemical treatment in which different chemicals are used to maintain the pH and other parameters of the wastewater. Sometimes oxidation process is also used for this purpose. Some highly reactive oxidizing agents are used like ozone [14]. The nascent oxygen liberated reacts with different chemical compounds to oxidize them. In case of phenolic compounds oxygen reacts with benzene ring and it converts into the aliphatic straight chain carboxylic acids. When industrialist calculate the comical effect it seems too much high [15].

On considering these drawbacks, some sorts of solution required more effective from these conventional methods and the operating should be lower. Electro chemical oxidation process is one of the best fits in this situation, a continuous running channel can be made with the wall of factory, [16-17] which can save the space and land.

#### 2. Materials and Methods

For the preparation of 100 ppm solution of 2-CP, 0.1 g of 2-CP have been taken and mixed with 1000 ml of distilled water. Solubility of 2-CP is low in water. To increase the solubility of ortho chlorophenol 0.2 ml of 1 ppm NaOH, solution has been added into the sample. After 30 min of stirring, neutralize the pH of the solution by using phosphoric acid. For electrolysis process some ions should be available in the sample so that electricity can pass through the solution and degrade the 2-CP in to aliphatic hydrocarbon. To obtain required results, 2 drops of 1 ppm solution of NaCl have been added into the standard solution. After that, 20  $\mu$ l of solution have been taken for testing purpose on the HPLC and find the absorbance.

Electrochemical method is being used to treat *o*chlorophenol and effect of different electrodes on the removal efficiency. The samples initially consist of 100 ppm solution *o*-chlorophenol. Samples treated for different timings as well as for same time at different voltages and the different electrodes, to study the removal efficiency in an electrolytic cell. Voltages are 5, 10, 15 and 20 volts. Electrolytic cell have made that it can contains 200 ml of sample water volume. Electrode dimensions are 0.0762 meter X 0.1016 meter. Time chosen for reaction is 5, 10, 15 and 20 minutes. 2 ml of 10 ppm salt solution is added for the conductance of electricity. HPLC / UV detector has been used for the quantitative analysis. Lambda max selected for Chlorophenol is 276 nm. With 1 ml/min flow rate of mobile phase (acetonitrile + water + methanol) with equal volume mixture the detection time is 11:35 min. Different concentrations of chlorophenol show different values of absorbance. Standard solutions of know concentration have been made and a reference calibration curve have been drawn to find the unknown concentrations of phenolic compound in treated water samples. By using Formula (1):

$$Y = m X + C \tag{1}$$

- Y = 5.0107 x + 0.5714
- Y = Absorbance (mAU) obtained the peak value
- m =Slope of line (5.0107)
- X = Value of concentration on X-axis (ppm of solution/ concentration of 2-CP in water)
- C = Y Intercept (0.5714)

Calibration curve helps to find the value of unknown concentration of solution. From these parameters one can calculate the degraded amount of 2-CP (2-Chloro Phenol) in water. Now subtract the reflected value from the standard value of master solution and again use the % age formula to calculate it.



Figure1. Calibration curve for 2-cholorophenole.

### 3. Results and Discussion

In accordance with the parameters studied graphite electrodes shows higher removal efficiency (Fig. 2) as compared to copper (Fig. 3) and copper shows better efficiency from iron electrode (Fig. 4). Voltage has directly proportional effect on the degradation of chlorophenol. As well as treated time & voltages have also direct relationship with efficiency. Iron electrode shows a different trend up to 7 min 10, 15 and 20 volts shows a similar efficiency and after that all trend lines show their liability separately (Fig. 4). 20 volts and 20 min operating time are the best conditions for degradation of 2-CP. Graphite & copper electrode (Fig. 2,3) shows less effective region 10-15 min operating time (other than 10 volts) in this time period, some side reactions start and the effectiveness of the process decreases. Iron electrode shows that a different trend in starting a steep line indicates the degradation reaction moving very fast (other than 5 volts).



Figure 2. Graphite Electrode.



Figure 3. Copper Electrode Efficiency.



Figure 4. Iron Electrode Efficiency.

# 4. Conclusions

Trends of graphs of experiments show that treated time and voltages have a direct relationship with the degradation of 2-CP. As time increases, the efficiency of this process increases. Same as voltage increase will show good results on the gradation up to 20 volts. Nature of electrodes has been also studied. As graphite is inert and semiconductor in nature, so its efficiency is much higher than copper and iron electrodes. Iron is a cheaper one, but its efficiency remains between the limit of 20% to 41.90% that is lesser than copper and graphite electrodes. Graphite electrode efficiency remains between the range of 35% to 60%. This means that graphite can show better results on lower voltages even 5 volts, 35% efficiency is greater than both copper & iron. Ultimately at 20 min and 20 volts the efficiency of the process goes to 60%. Copper electrodes show its efficiency in the limit of 28% to 51.85%. These results show that in a short time period for treatment and lower voltage the efficiency of copper electrode remains ineffective as compared to graphite electrodes for the industrial point of view. Copper has a higher market value as compared to iron. On the other hand the upper limit of the process shows the comparable results with respect to graphite electrodes. At 20 min of treatment time and 20 volts, the process shows its efficiency at 51.85%. The similar meaning of these results is on using 20 min residence time and 20 volts potential difference in process will remove 50% of the 2-CP from waste water. Iron electrodes when operated on 5 min and 5 volts the efficiency of the process comes about 20%.

While residence time increased up to 20 min as well as volts up to 20, the process shows its efficiency 41.9%. When we compare copper and iron electrodes from an industrial point of view copper rates in market ranges from 450 PRs/kg while iron rate is only 60 PRs/kg, which makes the maintenance and initial cost of the plant 86% cheaper than copper electrode plant. While on the efficiency basis, we can see there is only difference of 26%. This drawback can be covered by using 26% more iron electrodes in the process. Cost effect of these extra electrodes will be negligible. While using these type of arrangements we get the results of up to 51.85% degradation of 2-CP from the exhaust water of the industry. For optimized conditions and industrial solution combination of electrodes has to be used. 1st install Iron electrode and use 20 volts for 20 min treating time which shows about 41.9% removal of total concentration. Then use graphite electrode voltage 20 and treating time 20 min which shows the efficiency of 60%. This means that total 76.76% removal can be obtained within 40 min of residence time.

In this research work degradation of 2-chlorophenol has been studied. There are many parameters which affect the degradation reaction or support the side reactions. The effects of three parameters have been studied here. Parameters are given below;

- Treating Time
- Voltage
- Nature of Electrodes

Each parameter has a significant effect on the degradation process. But there are other parameters that are missing here; surface area, consequently the electric current density and concentration. The combination of these parameters along with above given three parameters can give the most optimal solution in the industry. Through these results we can reduce the operating time and operation cost as well. We can use alternate electrodes and their combinations. These arrangements can help us to reduce the reactor volume, installation and maintenance cost. Surface area and current densities should be studied with respect to the time, voltage and electrodes. The surface area can be increased by using perforated electrodes that not only reduce the pressure drop but also increase the degradation efficiency.

# References

- [1] Chen G., Electrochemical technologies in wastewater treatment, 2004. Sep. Purif. Technol., **38**(1), pp. 11–41.
- [2] Nguyen T. A., Juang R. S., 2013. Treatment of waters and wastewaters containing sulfur dyes: A review. Chem. Eng. J., **219**, pp. 109–117.
- [3] Lin S. H., Chen M. L., 1997. Treatment of textile wastewater by chemical methods for reuse. Water Res., 31(4), pp. 868–876.
- [4] Sripriya R., Chandrasekaran M., Subramanian K., Asokan K., Noel M., 2007. Electrochemical destruction of p-chlorophenol and p-nitro phenol -Influence of surfactants and anode materials. Chemosphere, 69(2), pp. 254–61.
- [5] Sala M., Gutiérrez-Bouzán M. C., 2014. Electrochemical treatment of industrial wastewater and effluent reuse at laboratory and semi-industrial scale. J. Clean. Prod., 65, pp. 458–464.
- [6] Körbahti B. K., Tanyolaç A., 2003. Continuous electrochemical treatment of phenolic wastewater in a tubular reactor. Water Res., **37**(7), pp. 1505–1514.
- [7] Cañizares P., Paz R., Sáez C., Rodrigo M. A., 2009. Costs of the electrochemical oxidation of wastewaters: A comparison with ozonation and

Fenton oxidation processes. J. Environ. Manage, **90**(1), pp. 410–420.

- [8] Article, P. A. N. A. T. of Contents, P. D. of A. 4-C. by S.-I. Polyoxometalates. Bin Yue S. J., Zhou Y., Xu J., Wu Z., Zhang X., Zou Y., 2002. Department of Chemistry, Fudan University, Shanghai 200433, Photocatalytic Degradation of Aqueous 4-Chlorophenol by Silica-Immobilized Polyoxometalates, pp. Environ. Sci. Technol., **36** (6), pp. 1325–1329.
- [9] Zhang W., Qu Z., Li X., Wang Y., Wu J., 2012. Je Sc Sc, 24(3), pp. 520–528.
- [10] Yoon J. H., Shim Y. B., Lee B. S., Choi S., Won M. S., 2012. Electrochemical degradation of phenol and 2-chlorophenol using Pt/Ti and boron-doped diamond electrodes. Bull. Korean Chem. Soc., 33(7), pp. 2274–2278.
- [11] Zhang F., Feng C., Li W., Cui J., 2014 . Indirect Electrochemical Oxidation of Dye Wastewater Containing Acid Orange 7 Using Ti / RuO 2 -Pt Electrode. Int. J. Electrochem. Sci., 9, pp. 943–954.
- [12] Jara C. C., Martínez-Huitle C. A., Torres-Palma R. A., 2009. Distribution of Nitrogen Ions Generated in the Electrochemical Oxidation of Nitrogen Containing Organic Compounds. Port. Electrochim. Acta, 27(3), pp. 203–213.
- [13] Zhang R., Zhang C., Cheng X., Wang L., Wu Y., Guan Z., 2007. Kinetics of decolorization of azo dye by bipolar pulsed barrier discharge in a three-phase discharge plasma reactor. J. Hazard. Mater, **142**(1–2), pp. 105–10.
- [14] Wang H., Wang J., 2007. Electrochemical degradation of 4-chlorophenol using a novel Pd/C gas-diffusion electrode, Appl. Catal. B Environ., 77(1-2), pp. 58–65.
- [15] Jamil T. S., Ghaly M. Y., El-Seesy I. E., Souaya E. R., Nasr R. A., 2011. A comparative study among different photochemical oxidation processes to enhance the biodegradability of paper mill wastewater. Hazard. Mater, **185**(1), 353-8.
- [16] Polcaro A. M., Palmas S., Renoldi F., Mascia M.,1999. On the performance of Ti/SnO2 and Ti/PbO2 anodesin electrochemical degradation of 2chlorophenolfor wastewater treatment. J. Appl. Electrochem., 29(2), pp. 147–151.
- [17] Torres R. A., Lovell T., Noodleman L., Case D. A., 2003. Density functional and reduction potential calculations of Fe4S4 clusters. J. Am. Chem. Soc., 125(7), pp. 1923–36.