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Photocatalytic Degradation of P-Cresol using Copper Chloride under UV – Irradiation

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ABSTRACT

Photocatalytic degradation of p-cresol was carried out using $CuCl_2$ under UV irradiation. The effect of photocatalyst loading, effect of photodegradation time of p-cresol and effect of pH were studied as variable parameters. The photodegradation rate constant and percentage photodegradation of p-cresol were calculated from the experimental results analysed using a UV-visible spectrometer after photoirradition with continuous stirring using set of magnetic stirrer respectively. The highest photodegradation of p-cresol was observed at 0.8g/L of $CuCl_2$ photocatalyst and 15.6ppm of p-cresol. Photocatalytic degradation was favorable in the pH of 7.49. The results confirm the fast degradation of p-cresol under photocatalytic regime. The percentage degradation was found to be 68.8% at concentration 15.6ppm. The average rate constant was found to be 1.9×10^{-3} mole/min. Based on the study of parameters, degradation was higher at pH of 8 and catalyst dose of 0.6g/L. Reusability shows no significant reduction in photocatalytic performance of the catalyst in photodegrading p-cresol.

Keywords: Degradation, p-cresol, Photocatalytic

INTRODUCTION

Pollution caused by hazardous substances has become a global concern. Therefore, semiconductor photocatalysis has become a topic of great interest mainly in view of its potential application in the decontamination of pollutants (Abdollahi *et al.*, 2012). Textile and dyestuff industries produce large amounts of wastewater containing various dye pollutants. Most azo dyes are non-biodegradable and their release into the environment poses a major threat to the surrounding ecosystems. Remediation of organic aquatic pollutants by photocatalytic oxidation has proven to be an attractive promising technology among the advanced oxidation processes. As one of the advanced oxidation processes (AOPs), it takes advantage of the ability of semiconductor photocatalyst to generate surface bound hydroxyl radical and trapped hole upon excitation by band gap light. Basically, under illumination by suitable light, this process (Equations 1–8) produces hydroxyl radical and hole which are powerful oxidants that can degrade a variety of organic compounds (Meenakshisundaram, 2019; Abdollahi *et al.*, 2012).

Photoexcitation: $SC + h\nu \rightarrow e- + h+$ (1)
Adsorbed oxygen: $(O_2)_{ads} + e^- \rightarrow O_2^{-\bullet}$ (2)
Ionization of water: $H_2O \rightarrow OH^- + H^+$ (3)
Protonation of superoxides: $O_2^{-\bullet} + H^+ \rightarrow HOO^\bullet$ (4)
$HOO^\bullet + e^- \rightarrow HO_2^-$ (5)
$HOO^- + H^+ \rightarrow H_2O_2$ (6)
$H_2O_2 + e^- \rightarrow OH^- + OH^\bullet$ (7)
$H_2O + h^+ \rightarrow H^+ + OH^\bullet$ (8)

The hydroxyl ($OH^\bullet$) radical is a powerful oxidant for degrading non selective organic compounds (Gratzel *et al.*, 1987; Peiró *et al.*, 2001; Abdollahi *et al.*, 2012). p-Cresol, also 4-methylphenol, is an organic compound with the formular $CH_3C_6H_4(OH)$. It is a colourless solid that is widely used intermediate in the production of other chemicals. It is a derivative of phenol, an isomer of o -cresol and m-cresol.P-Cresol is mainly consumed in the production of antioxidants, e.g., butylatedhydroxytoluene (BHT).

The monoalkylated derivatives undergo coupling to give extensive family of diphenol antioxidants. These antioxidants are valued because they are relatively low in toxicity and non-staining. p–cresol occurs naturally as a major component in pig odor, human sweat, human odour attractive to female mosquitoes. A temporal glands secretion examination showed the presence of phenol and p–cresol during mush in male elephants. Phenol and phenol derivatives are considered one of the most common organic water pollutants because of high toxicity, even at low concentrations. p-Cresol has been one of the very few compounds to attract the orchid bee Euglossacyanura and has been used to capture and study the species (Meenakshisundaram, 2019). Since, chemical industry wastewaters have high biological oxygen demand/chemical oxygen demand (BOD/COD), a number of pretreatment processes such as equaling/balancing, gravity adsorption or neutralization are available, and actual treatment can be achieved by chemical oxidation, ultra-filtration, adsorption, and biological or physico-chemical techniques. Selection of the appropriate method of treatment is influenced by a large number of factors related to each effluent characteristic, such as relative costs, levels of treatment required or site restrictions, etc. (Chen, *et al.*, 2006; Kandavelu, 2004; Lachheb, *et al.*, 2002). For example, biological and physico-chemical treatments are often used in tandem to obtain maximum removal of organics in chemical industry wastewater. The dual use of methods combats certain organics that are not biodegradable, as well as other organic constituents that may not be amendable to chemical precipitation. Among the several semiconductor photocatalysts used, TiO_2 has been considered the most superior in terms of suitability for application (Chen *et al.*, 2006; Kandavelu, 2004; Lachheb, 2002). The current interest in $CuCl_2$ is based on its high spectral response in UV region, which presumably, in some studies, resulted in higher efficiency of photocatalytic degradation (Shivaraman and Pandey 2000). The effective removal of p-cresol is currently an environmental problem (Gaya and Abdullah, 2008). Removal of organic materials was confirmed by x-ray photoelectron spectroscopy. In addition, it was found that photoluminescence from poly (3-hexylthiophene-2,5-diyl) (P_3HI) was quenched more by a $CuCl_2$ substrate after the UV-treatment (Figure 1). This suggested that on excitations, P_3HI were dissociated into carriers more efficiently on the UV-treated $CuCl_2$ substrate (Kamat, 2012). The authors attributed the higher photocatalytic activity of the modified catalyst to its large specific surface area ($275.7 m^2g^{-1}$), small particle size (8.1nm), high crystal quality and low electron-hole recombination factor.

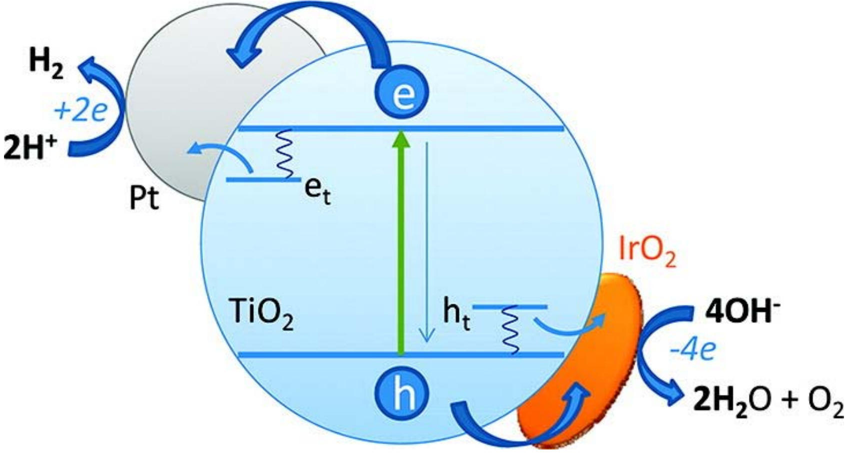

Figure 1: Schematic diagram of the charge transfer across semiconductor interface (Kamat, 2012).

Chen *et al.* (1998) applied mixture design and response surface techniques to prepare visible light-active TiO_2 photocatalyst which was co-doped with sulfur, carbon, and SnO_2. $Ti(OC_3H_7)_4$, $SnCl_4$ and thio urea were used as precursors. A synergic effect induced by the dopants SnO_2 and S, C on the visible light activity of TiO_2 was quantitatively established for the first time through mixture design techniques and response surface methodologies (Chen, *et al.*, 2006; Kandavelu, *et al.*, 2004). Generally, the degradation of phenolic compounds is known to yield genotoxic and carcinogenic intermediates such as catechol and hydroquinone which serious raise alarm. Jardim *et al.* (1997) have compared the toxicity of transient species of the degradation of pentachlorophenol, 2, 4-dichlorophenol and 2,3,5-trichlorophenol with those of the initial compounds. This work reported that the toxicity of the irradiated solution of pentachlorophenol to Escherichia coli could be higher than that of the starting material. In fact, even ordinary direct photolysis of frozen chlorophenols solution is known to yield more toxic intermediates (Blaha *et al.*, 2004). Similarly, increase in the toxicity of irradiated aqueous methyl parathion solution was observed in the presence of $CuCl_2$ which was attributed by Evgenidou *et al.* (2007) to the dissolution of zinc oxide during the Photodegradation process. Water solubility of p-cresol is over 21.5 g/L (25 °C). Thus, p-cresol can be a significant threat to surface water, groundwater sources, or generally the environment. It is imperative to investigate the effect of operating parameters such as: effect of photocatalyst loading, effect of time and effect of pH on degradation efficiency of p-cresol. Therefore, the research focuses mainly on using semiconductor photocatalyst ($CuCl_2$) in order to study p-cresol degradation under UV-irradiation. The investigation will provide information like organic percentage pollutant photodegradation and efficiency of degradation, rate constant of photodegradation, effect of time, pH, and catalyst loading.

EXPERIMENTAL

Preparation of solutions

The p-Cresol organic pollutant liquid (44.8ml) was accurately transferred into a standard flask (500ml) and diluted with deionized water till it reached the calibration mark to form a p-cresol solution of 2M. The p-cresol solution of (50ml) was transferred to another standard flask (100ml) and made to the mark with deionized water to form a p-cresol solution of (50ppm). The same procedure was repeated as above for the preparation of remaining concentrations which were; (40ppm, 30ppm, 20ppm, 10ppm). Dilute solutions of hydrochloric acid (0.1 M, 200cm^3) and sodium hydroxide (0.05M, 200cm^3) were also prepared from concentrated HCl [(36% (w/w); 1.18g/ml)] and NaOH pellets (97.5% w/w) pellets respectively (Abdollahi *et al.,* 2012).

Degradation of p-Cresol at various pH values

A 50ppm solution of p-Cresol was prepared in a 250ml and divided into 5 different beakers of equal volume. 2M hydrochloric acid and 0.5M sodium hydroxide were employed for pH adjustments to 5, 6, 7, 8 and 9 respectively**.** 2.0 g of $CuCl_2$ was added into p - cresol solutions, and placed under UV-irradiation. Meanwhile, aliquot sample of solution were collected in order to get initial concentration (C_O), after 120 min final concentration (C_t) were collected. The samples were filtered using Whatmann filter paper and, analyzed by using validated UV-Spectrophotometer (Spectrumlab. 752S, England) within the wavelength of UV- 224nm. Same procedures were used on the remaining samples respectively (Abdollahi *et al.,* 2012).

Effect of photocatalyst on the degradation of p-Cresol

From the calibration curve, (50ppm) solution of p-Cresol as an optimum concentration was prepared and divided into 4 in different beakers of equal volume. 0.2g, 0.4g, 0.6g, 0.8g photocatalyst was weighed and introduced into the solutions, and placed under UV-irradiation. Meanwhile, aliquot sample of solution were collected in order to get initial concentration (C_O), after 120 min final concentration (C_t) were collected. The samples were filtered using Whatmann filter paper and, analyzed by using validated UV-Spectrophotometer within the wavelength of UV- 224nm. Same procedures were used on the remaining samples respectively (Abdollahi *et al.,* 2012).

Effect of time on the photodegradation of p-cresol

From the calibration curve, (50ppm) solution of p-Cresol as an optimum concentration was prepared and 0.5g/l of photocatalyst ($CuCl_2$) was introduced into the working solution and were placed under UV-irradiation. Aliquot of sample solution were collected at regular time interval (10, 20, 30, 40, 60, 70, 80 and 120 minutes) respectively. The samples were filtered using Whatmann filter paper and were analyzed by validated UV-spectrophotometer (Abdollahi *et al.,* 2012).

Percentage Photocatalytic degradation

The percentage photocatalytic degradation of p-cresol was calculated using equation 9:

$$photodegradation\,(\%) = \frac{(C_o - C_t)}{C_o}\,x\,100 \qquad (9)$$

Where: C_0 = initial concentration of p-cresol, C_t = concentration of p-cresol after photo irradiation. All photocatalytic degradation experiments were carried out in duplicate (Abdollahi *et al.,* 2012).

Estimating rate constant of Photocatalytic degradation of p-cresol

The rate constant of photocatalytic degradation of p-cresol was calculated using equation 10.

$$\ln(Ct/Co) = kt \,\ldots\ldots\ldots(10)$$

where: Co = initial concentration of p-cresol, Ct = concentration of p-cresol after photoirradiation, k = constant, and t= time taken in degradation.

RESULTS AND DISCUSSION

According to Beer's Law, A = αbc, under ideal conditions, a substance's concentration and its absorbance are directly proportional: hence the law was employed to determine the concentration of p-Cresol after the photodegradation process.

Effect of Photocatalyst Loading

A series of experiments were carried out by varying the amount of catalyst (0.2, 0.4, 0.6 and 0.8 g/L) respectively to establish the effect of photocatalyst loading and to avoid unnecessary excess photocatalyst. The percentage of photodegraded p-cresol as a function of irradiation time was plotted in Figure 2. The maximum percentage (3.5%) of photodegradation was obtained at 0.8g/L of photocatalyst. This is due to the increase in number of active sites with increasing photocatalyst loading which consequently leads to enhanced production of •OH radicals.

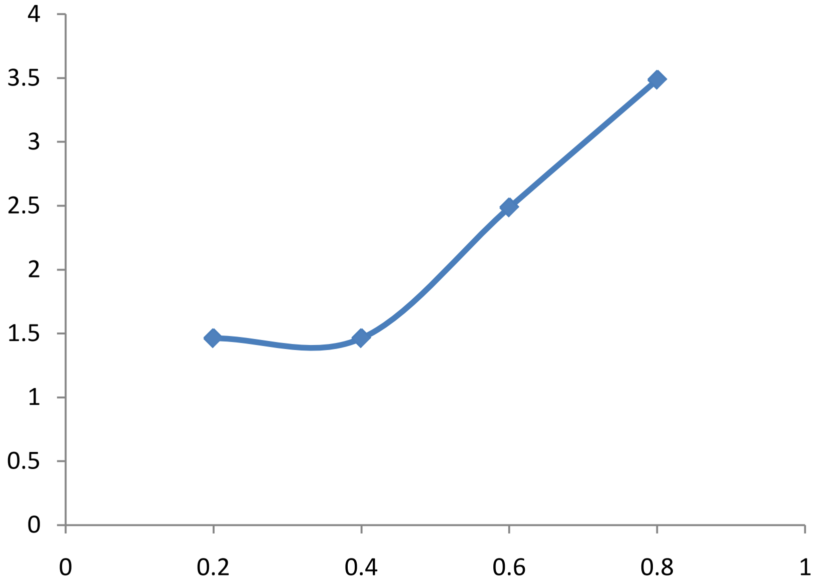

Figure 2: Effect of photocatalyst loading on photodegradation of p-Cresol

Moreover, the number of adsorbed p-cresol molecules was increased owing to an increase in the number of photocatalyst particles, which causes increasing photodegradation (Fox *et al*., 1993). When the amount of photocatalyst was enhanced beyond optimum, however, photodegradation was not increased. The decreased efficiency beyond the optimum photocatalyst loading may be attributed to the screening effect of excess photocatalyst particles in the solution (Pardeshi *et al*., 2008). Furthermore, agglomeration and sedimentation of photocatalyst particles is also possible (Konstantinou *et al*., 2004). In such a condition, a part of the photocatalyst surface probably becomes unavailable for photon absorption and o-cresol adsorption, thus bringing little stimulation to the photocatalytic reaction.

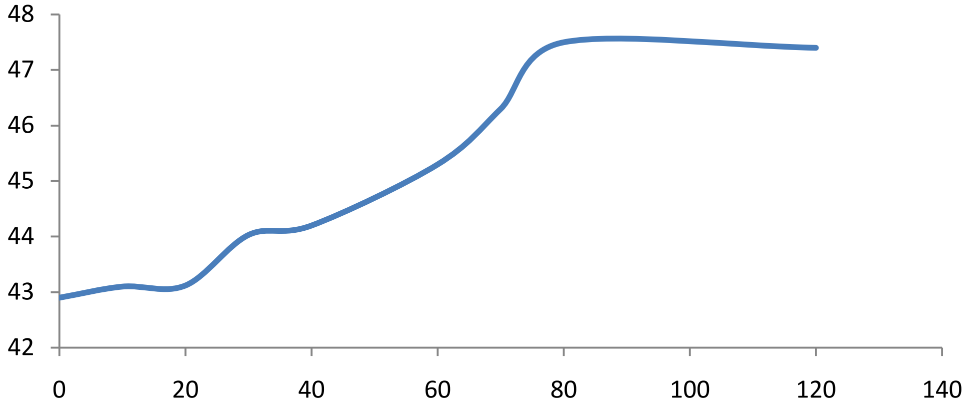

Figure 3: Effect of Time on photodegradation of p-Cresol

Initially, there is an increase of degradation with the increases of time until the equilibrium time was reached at about 80 minutes after which no further degradation was observed as shown in Figure 3.

Effect of pH

It is important to study the effect of pH in the photodegradation of p-cresol because the charge of $CuCl_2$ surface and p-cresol vary with shift in pH. At low pH $CuCl_2$ surfaces adsorb protons to produce positively charged surfaces. At high pH (usually above pH 9) they lose protons to produce negatively charged surfaces.

At pH values below 5.0, only small significant change in degradation was recorded. The $CuCl_2$ powder was fully dissolved into solution. The percentage degradation has rapid increases at pH value above 5.0 till it reaches the pH value 7.45 at which, the degradation starts to decrease. This means, it is attaining the optimum point. Most organic compounds are removed on or near the surface of photocatalyst; therefore the activity of photocatalyst seriously depends on adsorption of amount of pollutant over photocatalysis (Abou-Helal *et al.*, 2002; Anandan *et al.*, 2007). Increasing photodegradation may be due to the increase in adsorption of p-cresol on the photocatalyst surface. Increasing adsorption may be due to a decline of the electrostatic repulsive forces and increased interaction between photocatalyst surface (pH_{zpc} = 9) (Kosmulski, 2006) and p-cresol because with increasing pH the number of positive species (p-cresol - H^+) decreases.

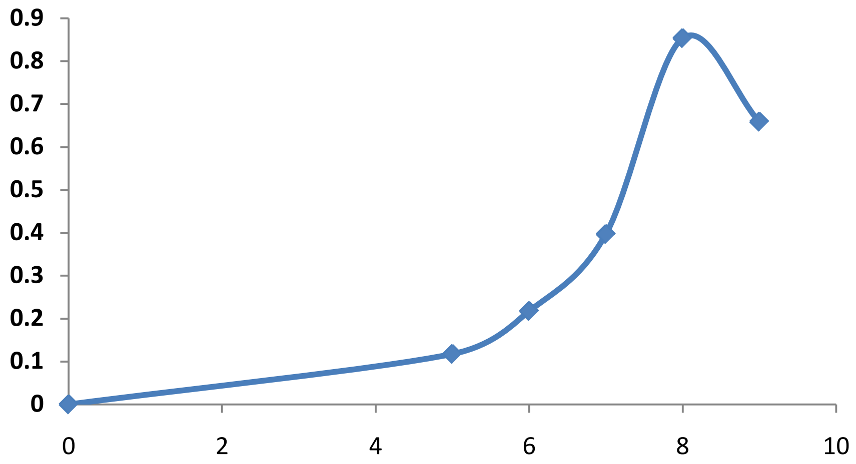

Figure 4: Effect of pH on photodegradation of p-Cresol

Photocatalytic degradation of p-cresol was investigated in the absence of photocatalyst at pH 8. Results show only 6% of p-cresol was photolysed in the absence of photocatalyst (Figure 4). Therefore, p -cresol is relatively stable under UV irradiation.

Photocatalytic degradation of p-cresol was investigated in the absence of photocatalyst and at pH of 7.49. Table 1 shows the dissipation of p-Cresol at various concentrations and different time in which. The result confirms the fast degradation of p-cresol under photocatalytic regime. The highest % degradation was found to be 68.8% at concentration15.6ppm, pH of 8 and catalyst dose of 0.85g/l. The average rate constant was found to be 1.9 x 10^{-3} mole/min.

Table 1: Dissipation of p-Cresol at various concentrations and different time

Time (Minutes)	Concentration (ppm)	% Degradation	Rate Constant
0	32.8	0	0
10	29.6	40.8	2.4 x 10^{-3}
20	28.3	43.4	9.3 x 10^{-3}
30	27.1	45.8	0.4 x 10^{-3}
40	24.1	51.8	8.2 x 10^{-3}
60	22.8	54.8	3.0 x 10^{-3}
70	15.6	63.2	4.2 x 10^{-3}
80	13.6	68.6	4.5 x 10^{-3}
120	15.6	68.6	9.7 x 10^{-3}

CONCLUSION

Photocatalytic degradation appears to be a promising technology that has a number of applications in environmental systems such as air purification, water disinfection, hazardous waste remediation, and water purification. In addition, the basic research that underlies the application of this technology is forging a new understanding of the complex heterogeneous photochemistry of metal oxide systems in multiphasic environments. Using photocatalytic degradation under UV light a convincing dissipation of organic pollutant (p-Cresol) in a favorable time was achieved. The following parameters were determined which include; a pH of 8, catalyst dose of 0.8g/l, and time of 80 minutes. Therefore, in the treatment of waste water containing p-Cresol, the photocatalytic reactor should be designed in such a way that, the retention time is 80 minute. Hydrogen peroxide is formed on illuminated $CuCl_2$ surfaces in the presence of air via dioxygen reduction by a conduction-band electron in the presence of a suitable electron donor.

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