PHOTOCATALYTIC DEGRADATION OF META-CHLOROPHENOL USING SOLAR AND ARTIFICIAL RADIATION

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ABSTRACT

The objective of present article is to study the photocatalytic degradation (PCD) of m-chlorophenol present in pharmaceutical wastewater and to avoid the future accumulation of m-chlorophenol in aquatic environment. The degradation of m-chlorophenol of was investigated in presence of commercially available Degussa P-25TiO_2photocatalyst and solar radiation as well as artificial UV irradiation. The effect of different operating parameters like initial concentration of m-chlorophenolcatalytic loading, pH of solution, effect of anion and cations on PCD of cipro have been investigated in detail. It was observed that as initial concentration of m-chlorophenol increase rate of PCD decreases. Optimum catalytic loading was observed at 1 g/L for m-chlorophenol concentration 0.1gm/l. The influence of pH on the PCD of m-chlorophenol was studied at pH ranging from 3 to 11 and it was found that maximum degradation rate was observed at 9 pH. From kinetic studies, it was found that the PCD obeys pseudo-first order kinetics with reaction rate constant K_{app} = 0.02315 min^{-1}. Pseudo first order rate expression of Langmuir–Hinshelwood as follows.

$$r = -\frac{dC}{dt} = K_{app} C$$

I INTRODUCTION

The rapid growth of the world's population has created an increase in the demand for the Earth's limited supply of freshwater. Thus, protecting the supply of water and addressing concerns such as toxicity and the presence of chemicals that may have potential long term adverse human and ecological effects has become an important issue. Pharmaceuticals and personal care products enter the environment at low concentrations primarily as metabolites excreted by humans and animals or in effluents that are disposed into wastewater from hospitals, pharmacies, and chemical manufacturing facilities. Once these compounds reach wastewater treatment plants, they are not completely removed and presence m-chlorophenolof in aquatic environments may cause serious threats to the ecosystem and human health [3, 4].

Therefore there is a need to develop eco-friendly, cost effective technique for the treatment of pharmaceutical wastewater. The studies have shown that advanced oxidation processes (AOP) and adsorption are viable treatment methods for completely removing m-chlorophenolfrom water and wastewater. Recently, extensive

studies have been performed on the degradation of toxic organic compounds in waste water via modified semiconductor photocatalyst [5].

The purpose of this article is to investigate the photocatalytic degradation (PCD) of m-chlorophenol using Degussa P-25 TiO_2photocatalyst and using solar and artificial radiation. The effect of various operating parameters such as initial concentration of m-chlorophenol ,photocatalyst loading, pH of solution and effect of presence of co-exiting ions on photocatalytic oxidation of m-chlorophenol have been studied in order to establish the optimum process parameters. The kinetics of photocatalytic oxidation has been also studied

II MATERIAL AND METHODS

2.1 Reagent

Aroxide Degussa P-25 TiO_2 (70:30% w/w anatase to rutile) with an average particle size of 30 nm and BET surface area about 55 $m^2 g^{-1}$ was used as the photocatalyst. . Acetic acid (CH_3COOH), Acetonitrile, Na_2CO_3, NaCl and $(NH_4)_2SO_4$ were purchased from Merck India Pvt. Ltd, Mumbai, India. The different concentration aqueous solution m-chlorophenol was prepared in de-ionized water (DI Water) was used as pollutant.

2.2 Equipment

A parabolic reflector with surface area of 1.5 m^2 was used for concentration of solar radiation.The pH of aqueous solution of ciprofloxacin HCl was monitored by using pH meter of Thermo scientific Orion star model. Plain solar radiation intensity was measured in W m^{-2} by 'daystar meter' (daystar Inc, Las Cruces, NM, USA) working on the photocell principle. Solar radiation intensity at ground level is referred to as plain intensity henceforth. Average solar intensity of solar irradiation was found approximately 800 watts/m^2. Experimental setup is as shown in Fig no.2. Deionized water (Millipore Milli-Q system) was used to prepare aqueous solutions of ciprofloxacin HCl. Cooling media (water) was circulated by chiller (Julabo).

2.3 PCD Experiment

An annular borosilicate glass reactor as shown in Figure 2 was used as photocatalytic for performing the photocatalytic oxidation reaction. The de-ionized water (Millipore Milli-Q system) was used to prepare aqueous solutions of m-chlorophenol. The temperature of reaction mixture was kept constant by circulated the chilled water through the annular space between the lamp via JULABO chiller FP-50 MA. In each experiment 500 ml of solution was charged in the reactor. An air at rate of 1 L min^{-1} required for oxidation reaction and to keep all the TiO_2 in suspension was supplied via ring sparger located at the bottom of the reactor. In the photocatalytic experiments Degussa P-25 TiO_2 was used as the photocatalyst. The solution was equilibrated by stirring for 15 minutes in the dark before exposing the reactor assembly to the solar radiation. The liquid samples were taken periodically from the reactor for analysis and stored in amber colored bottle. During the PCD experiments the pH of the solution was not controlled. Same experimental procedure was carried out by using artificial radiations. A visible tungsten lamp with power input 400 watts was used as the source of artificial radiations.shown in fig.1

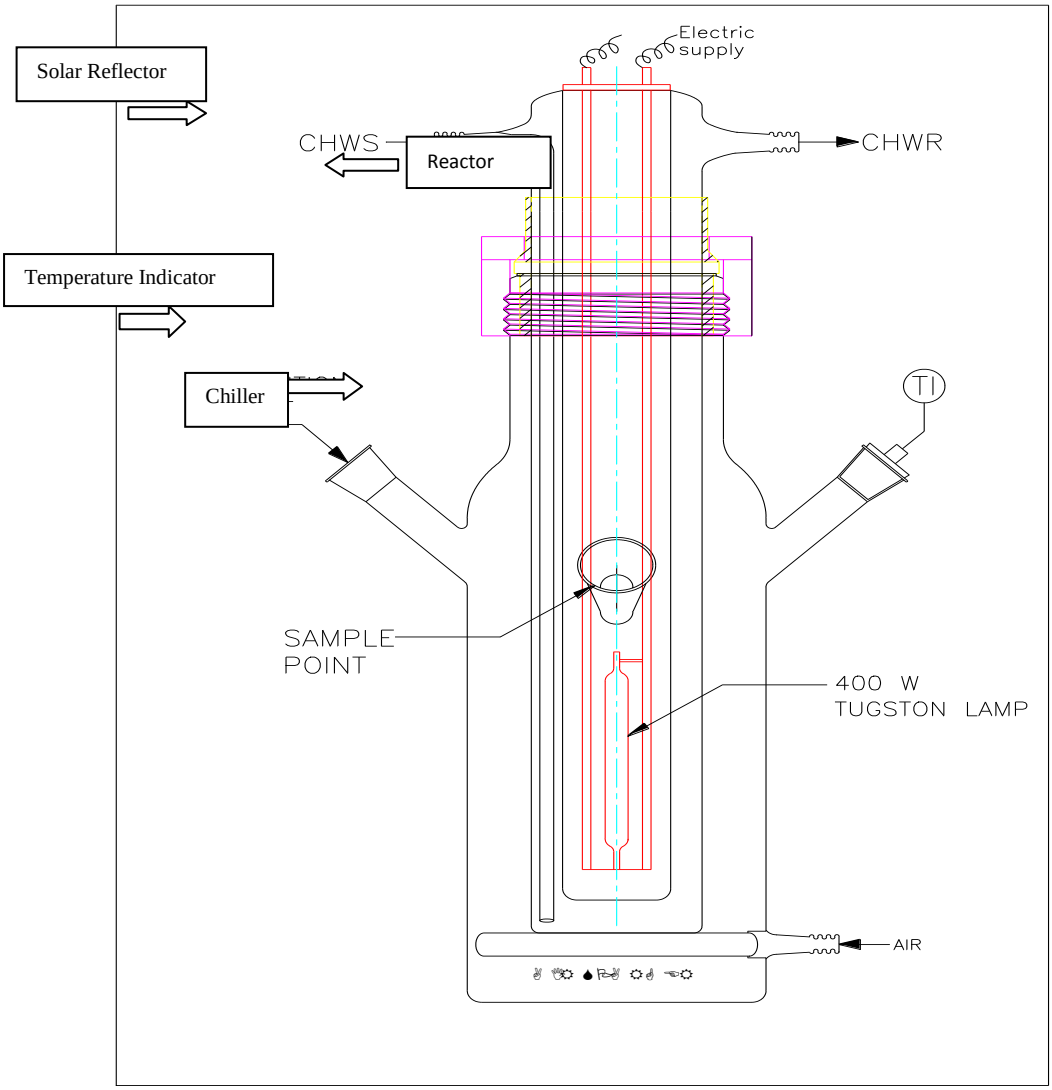

Fig 1: 9 Photocatalytic Reactor for Artificial Method

Figure 2: Experimental tup of photocatalytic degradation of meta-chlorophenolusing solar radiations.

III RESULTS AND DISCUSSION

3.1 Initial Concentration Effect

Initial concentration of pollutant is the important parameter that affects the rate of PCD of pollutant. The experiments on PCD of meta-chlorophenolwere conducted for solutions with range of 0.1gm/l – 1 gm/l concentrations. It was found thatmeta-chlorophenolof initial concentration50 mg/l was completely degraded within2 hr by using solar radiations. The PCD time increased with increase in meta-chlorophenolconcentration. In this particular study catalyst concentration was kept constant 1 gm/l. The concentration ofmeta-chlorophenolhas a significant effect on the PCD. The rate was higher when the initial concentration meta-chlorophenolwas less. This can be explained as for a certain TiO_2 concentration, the amount of active centers on the photocatalyst was finite, so PCD rate was fast with low concentration ofmeta-chlorophenol. The PCD rate decreases when the concentration of increases, possibly because the molecules ofmeta-chlorophenol was excessive in comparison with the amount of active centers on the photocatalyst. Figure shows the effect of initial concentration ofmeta-chlorophenol on rate of PCD. The photocatalytic process was influenced by the initial concentration ofmeta-chlorophenolA linear relationship was observed between meta-chlorophenolconcentration and irradiation time, as shown in Figure 2.

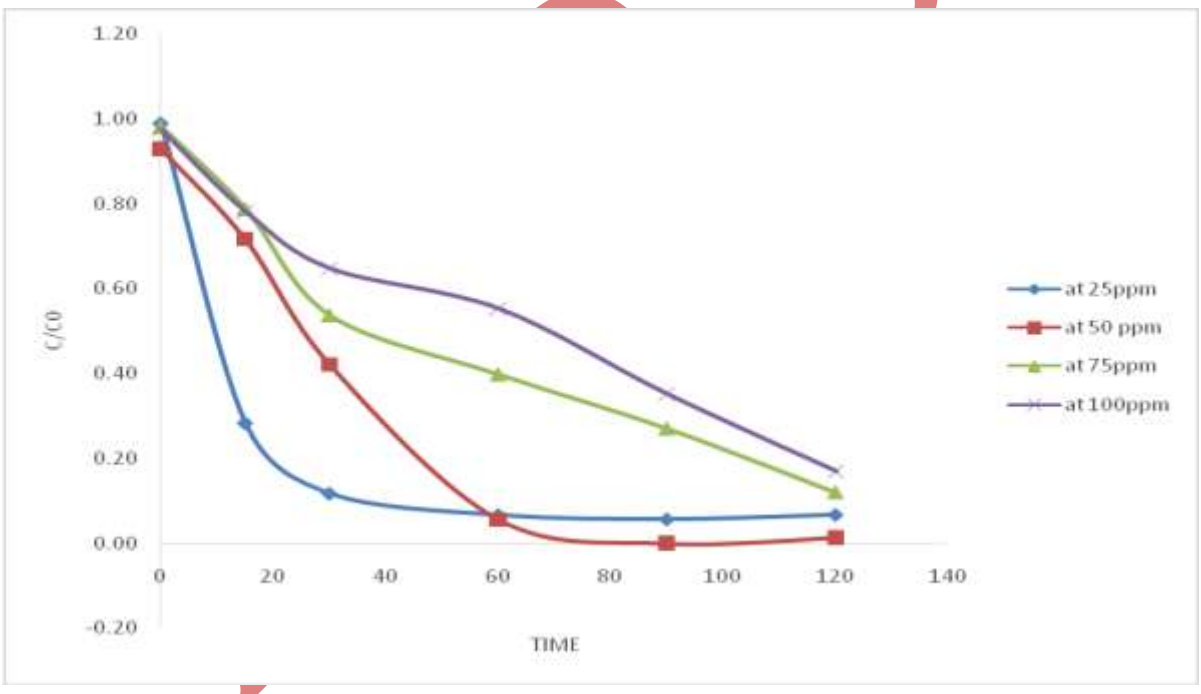

Figure 2: Effect of initial concentrations of meta-chlorophenolunder solar radiation.

3.2 Effect of catalyst concentration on rate of degradation

The concentration of TiO_2 is a critical parameter in photocatalytic oxidation. It affects on the reaction rate and consequently on the cost of treatment. The effect of catalyst loading of photocatalyst was studied on 0.1 gm/l of aqueous solution of ciprofloxacin HCl. The range of catalyst loading was 0 to 2 gm/l. It was observed that the pH of solution was 5.8 during this particure.

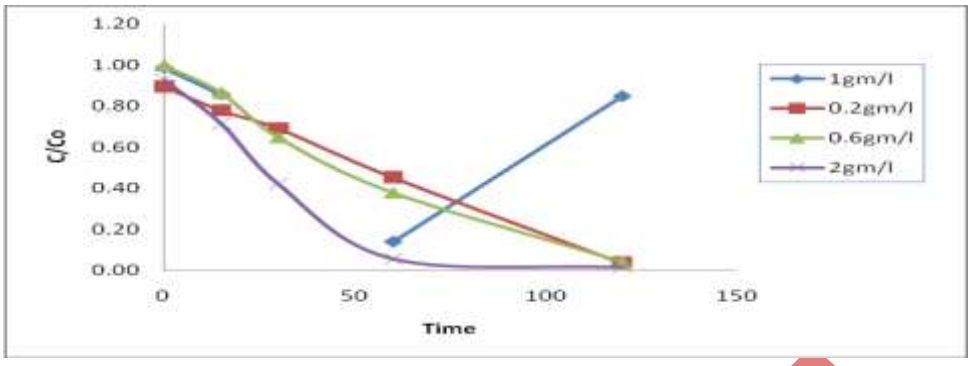

Figure 3: Effect of catalytic TiO_2 on meta-chlorophenol degradation using solar radiation.

3.3 Effect of pH of solution on degradation of meta-chlorophenol

Waste water from different industries contains different pH so it is an important parameter that affects the rate of degradation. The PCD of m-chlorophenol does not depend only on TiO_2 concentration but also on pH value of m-chlorophenol solution, since it determines the surface charge properties of the photocatalyst and therefore the adsorption behavior of the organic substrate. In the present work, the influence of pH on the degradation of m-chlorophenol in aqueous suspensions of $TiO_2$was studied at pH ranging from 3 to 11. Figure shows the degradation of m-chlorophenol at different pH with respect to time. The pH values were adjusted by adding aqueous solutions of 0.1N HCl and 0.1 N NaOH to get a desired pH value. Initial concentration of m-chlorophenol was 0.1 gm/l and catalyst loading was 1 g/l in these experiments.

It was observed that PCD of m-chlorophenol was faster in weak basic (pH 9) than those in weak acidic (pH 5) or strong alkaline (pH 11) conditions [6]. It shows that the rate PCD of m-chlorophenol is strongly influenced by the reaction pH. The TiO_2 surface will remain positively charged in acidic medium (pH < 6.25) and negatively charged in alkaline medium (pH > 6.25) because of that reason under acidic condition (3 pH), m-chlorophenol is positively charged which is same as TiO_2 surface resulting in repulsion between them. Cl^- may compete with water molecules for the adsorption on TiO_2 surface this blocks the active sites of TiO_2 and hence production of hydroxyl radical decreases. Both TiO_2 and m-chlorophenol are negatively charged under strongly basic conditions (pH 11) which causes repulsion between them and lowers the PCD. Effect of pH on rate of degradation is as shown in Figure5. It was observed that at pH 9 rate of degradation was maximum.

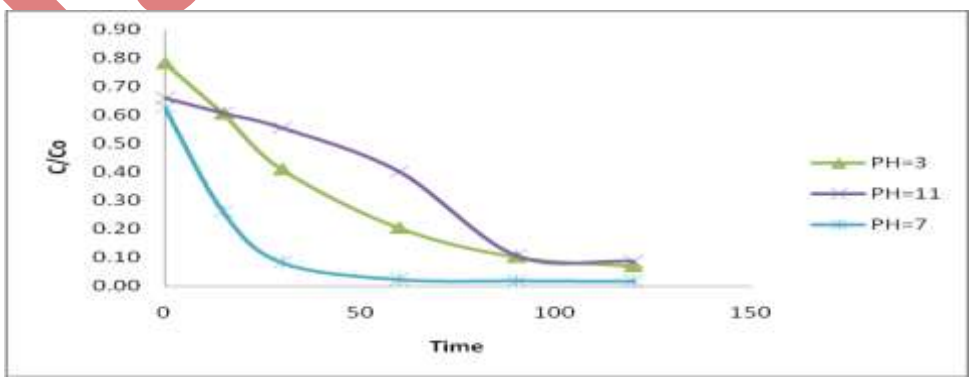

Figure 4: Effect of pH on Rate of degradation of m-chlorophenol using solar radiation.

3.4 Effect of co-existing ions

The presence of certain inorganic ions in the reaction medium has a significant effect on degradation of pollutants. The effect of sodium carbonate, sodium chloride and ammonium sulphate on degradation m-chlorophenol was studied. During this experiment salt concentration was 0.5 gm/l. m-chlorophenol concentration was 0.1 gm/l. and 2 gm/l of TiO_2 was suspended for 120 min of radiation sodium carbonate show less degradation as compared to other salts. For 120 min run of salt addition experiment shows lower PCD rate of m-chlorophenol than that of solution without salt as shown in Figure 6.

For SO_4^{2-} ions, they are adsorbed in the surface of TiO_2 and consequently react with photo-induced holes (h+)

$$h^+ + SO_4^{2-} \rightarrow SO^{-\bullet}$$

As 'S' is the strong oxidizing agent, the sulfate radical can accelerate the reaction and participate in the degradation.

For NaCl it reacts with m-chlorophenol to form other side product or it improves the adsorption of m-chlorophenol on surface of TiO_2. Na_2CO_3 has hindrance effect which reduces the m-chlorophenol adsorption onto the catalyst surface which results into the decreased PCD of m-chlorophenol.

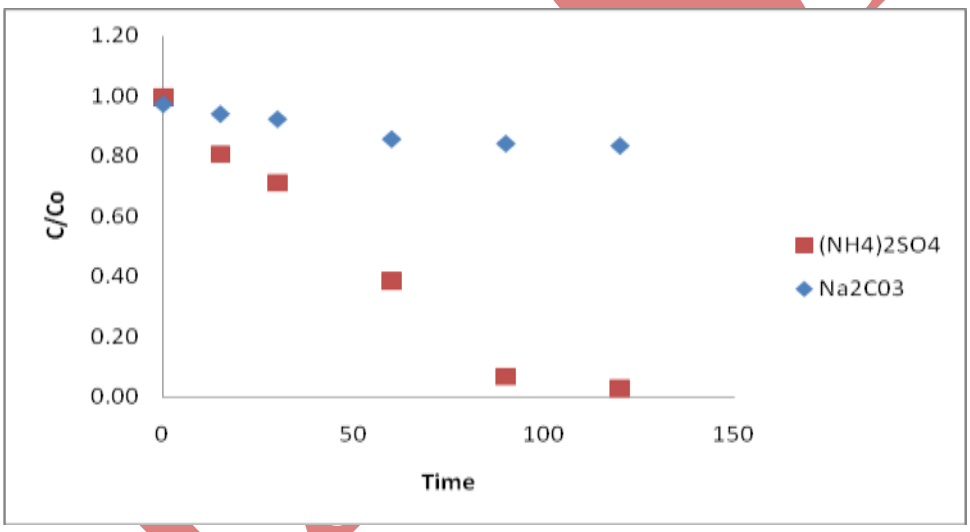

Figure 5: Effect of Salt Addition on Rate of degradation of ciprofloxacin HCl using solar radiation.

IV KINETIC MODELS OF PHOTOCATALYTIC OXIDATION OF M-CHLOROPHENOL

Langmuir–Hinshelwood rate expression has been successfully used for heterogeneous photocatalytic degradation to determine the relationship between the initial degradation rate and the initial concentration of the organic substrate. The Langmuir–Hinshelwood model was developed to describe gas–liquid reaction it is widely used for liquid–solid reactions. Reaction kinetics gives information about the reaction rates and the mechanisms by which the reactants are converted to the products.

PCD proceed on the surface of semiconductor via several steps. In this model, the reaction rate (r) is considered to be proportional to the surface fraction covered by the substrate (θ).

$$-\ln\left(\frac{C}{Co}\right) = Kapp * t$$

Where, Co is initial concentration of m-chlorophenol. A plot of $-\ln\frac{C}{Co}$ against t and slope of linear regression analysis is equal to the value of K_{app}.

A plot of $-ln\frac{C}{Co}$ versus t for all the experiments with different initial concentration of m-chlorophenol is shown in Figure and Figure. The values of K_{app} were obtained directly from the regression analysis of the linear curve in the plot. The results showed that K_{app} decreased from 0.102 to 0.01 min^{-1} and 0.144 to 0.017 min^{-1} when m-chlorophenol initial concentration increased for artificial radiation and solar radiation respectively. Regression coefficients are more than 0.96, it shows good fitting of data.

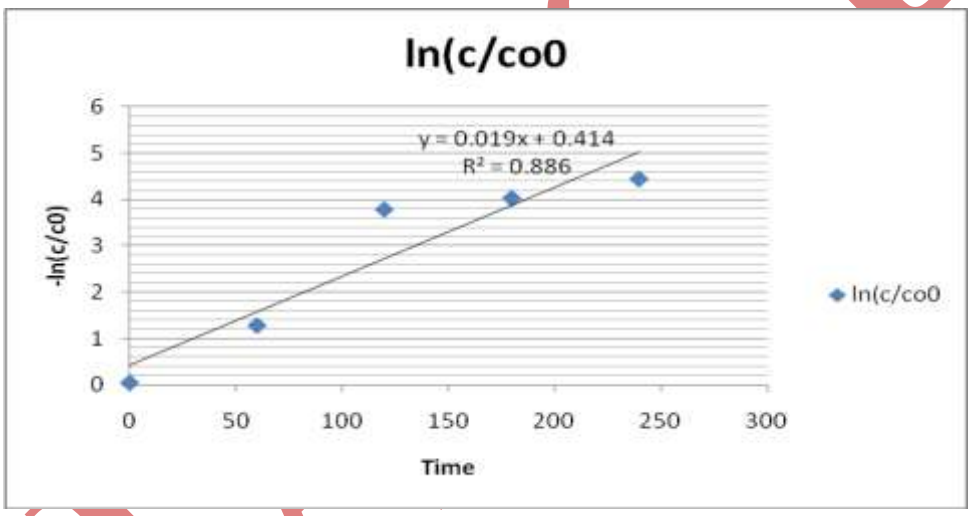

Fig.6.Effect of initial concentration of ciprofloxacin HCl under artificial radiation with respect to time.

Table 1: Regression coefficients (R^2) and K_{app} for initial concentration of m-chlorophenol under artificial radiation and solar radiation.

Initial Conc. Of Ciprofloxacin HCl	Solar radiation		Artificial radiation	
	K_{app} (1/min)	R^2	K_{app} (1/min)	R^2
100 mg/l	0.027	0.92	-	-
300 mg/l	0.026	0.95	-	-
500 mg/l	0.022	0.90	-	-
1000 mg/l	0.037	0.956	0.022	0.86

The effect of initial concentration of m-chlorophenol on PCD rate was studied by using solar and artificial radiation Table 1 shows the R^2 and Kapp for artificial and solar radiation, from this Table it was found that Kapp decreases as concentration of m-chlorophenol increases, but rate constant for solar radiation is much higher as compare to artificial radiation.

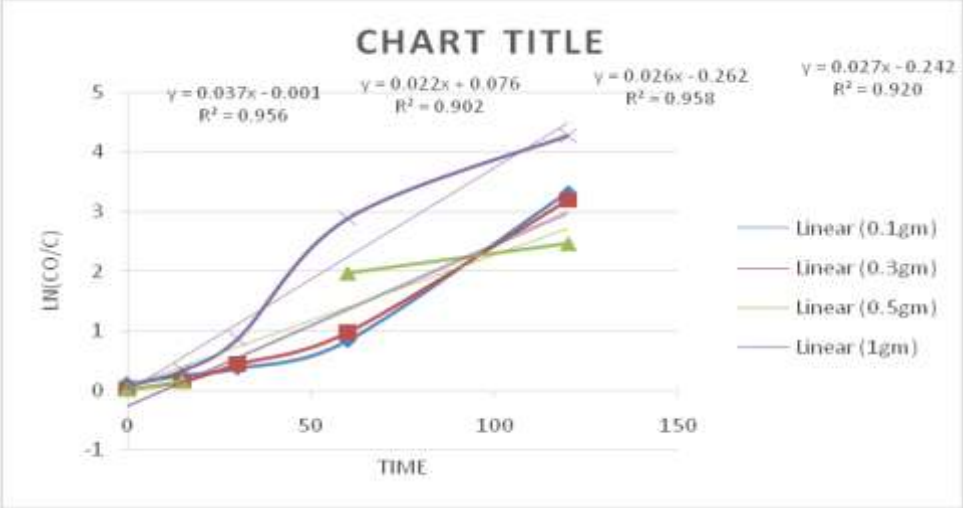

Figure 7: Effect of initial concentration of m-chlorophenol under solar radiation with respect to time.

V CONCLUSIONS

PCD of m-chlorophenol using solar and artificial radiation in the presence of TiO_2photocatalyst was successfully accomplished. In this investigation it was found that K_{app} in the presence solar radiation is much higher than that of artificial radiation. This indicates that solar radiations are much more effective as compared to artificial radiations. Effect of various operating parameters on PCD of m-chlorophenol was studied and it was observed that PCD rate was maximum at pH 9. The effect of sodium carbonate, sodium chloride and ammonium sulfate on PCD of m-chlorophenol was studied and it was found that all three salts (NaOH, NaCl, $(NH_4)_2SO_4$) has no significant effect on the rate of PCD as compared without salts. The optimum catalytic loading was observed for 1 gm/l. From this article it can be concluded that solar radiations are significantly effective than artificial radiations for PCD of m-chlorophenol

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