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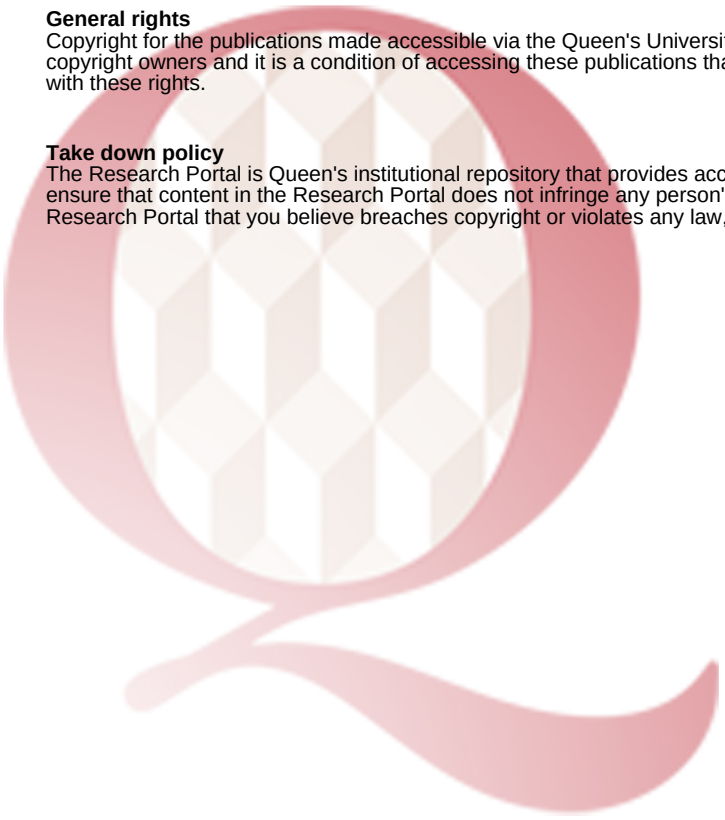

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Phenol degradation by powdered metal ion modified titanium dioxide photocatalysts

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Abstract

Conventional water purification and disinfection generally involve potentially hazardous substances, some of which known to be carcinogenic in nature. Titanium dioxide photocatalytic processes provide an effective route to destroy hazardous organic contaminants. This present work explores the possibility of the removal of organic pollutants (phenol) by the application of TiO_2 based photocatalysts. The production of series of metal ions doped or undoped TiO_2 were carried out via a sol gel method and a wet impregnation method. Undoped TiO_2 and Cu doped TiO_2 showed considerable phenol degradation. The efficiency of photocatalytic reaction largely depends on the photocatalysts and the methods of preparation the photocatalysts. The doping of Fe, Mn, and humic acid at 1.0 M% via sol gel methods were detrimental for phenol degradation. The inhibitory effect of initial phenol concentration on initial phenol degradation rate reveals that photocatalytic decomposition of phenol follows pseudo zero order reaction kinetics. A concentration of >1 g/L TiO_2 and Cu doped TiO_2 is required for the effective degradation of 50 mg/L of phenol at neutral pH. The rise in OH^- at a higher pH values provides more hydroxyl radicals which are beneficial of phenol degradation. However, the competition among phenoxide ion, Cl^- and OH^- for the limited number of reactive sites on TiO_2 will be a negative influence in the generation of hydroxyl radical. The dependence of phenol degradation rate on the light intensity was observed, which also implies that direct sunlight can be a substitute for the UV lamps and that photocatalytic treatment of organic pollutants using this technique shows some promise.

Keyword: Photocatalysts; Modified titanium dioxide; Photoreactor; Sol gel method; Wet impregnation method; Phenol;

1- Introduction

While the world's population tripled in the 20th century, the use of renewable water resources has grown six-fold. Poor access to good quality drinking water increases the risk of waterborne diseases, which result in more than 10 million deaths. Diarrhoea alone is responsible for 2.2 million deaths each year, mostly among children under the age of five. This represents a significant global problem, however a number of options available today for water disinfection include chlorination, ozonation, iodine treatment, UV treatment, and boiling [1]. The ideal solution would offer complete and full sterilization, without harming other forms of life; it should also be inexpensive as well as non-corrosive [2].

The last 20 years has seen the development of two of the most interesting disinfection alternatives: solar disinfection and TiO_2 photodisinfection under UV illumination [3]. The combination of the two methods would result in a much greener, cheaper, more efficient, less energy consuming technology, which could be produced and widely applied whilst causing no harm to human health. Considering the fact that the areas of the world that lack access to safe drinking water, which are also the world's poorest nations, have an abundance of sunlight irradiation, the provision of this new technique can alleviate the current burden on the global water supply and improve sanitation. However, the band-gap of TiO_2 is large, and is only active in the ultraviolet region (<400nm), which is < 10% of the overall solar intensity, therefore the light harvesting ability of TiO_2 is very limited [4]. The challenges in this area are the development and mechanism investigation of an efficient TiO_2 based photocatalyst, which is workable under sunlight [5]. Among many catalyst improvement techniques, doping has been shown to be one of the most promising options, however its application in water disinfection requires further investigation. Current photocatalysis is mainly focused on TiO_2, and the basis for

its use is the employment of sunlight (or an artificial solar simulator lamp system) as an energy input so that TiO_2 can be photoactivated by the UV spectrum of the irradiation [6].

The work of Matsunaga et al. [7] showed that TiO_2 was effective in photokilling *Lactobacillus acidophilus* (gram-positive bacteria), *Saccharomyces cerevisiae* (yeast) and *Escherichia coli* (gram-negative bacteria) under a metal halide lamp (12000 $\mu e \cdot m^{-2} \cdot s^{-1}$) for 1-2 h, moreover a mechanism involved in the photooxidation of CoA was proposed. Ireland et al. [8] found that the addition of electron acceptor-hydrogen peroxide at millimolar level had a positive impact on the disinfection capability. Ide et al. [9] reported that the presence of deposited Au on the supported layered TiO_2 could significantly improve its photocatalytic activity in the visible light range. Zhang et al. [10] found that the absorption edge of N,S-codoped TiO_2 had a red-shift and possessed the photocatalytic efficiency under visible light. Li et al. [11] proposed a visible semiconductor sensitizer BiOI, which exhibits excellent photocatalytic activities on the degradation of phenol under visible light irradiation. Photocatalytic tests showed that BiOI is an effective sensitizer for improving the visible light photocatalytic activity of TiO_2. Zhu et al. [12] investigated the photocatalytic disinfection of E. coli 8099 using Ag/BiOI composites under visible light irradiation. The experimental results showed that the photocatalytic disinfection efficiency of E. coli (5×10^7 cfu mL^{-1}) using 2.09%Ag/BiOI was almost 99.99% within 10 min irradiation. Photocatalytic silver doped titanium dioxide nanoparticles (nAg/TiO_2) were investigated for their capability of inactivating bacteriophage MS2 in aqueous media [13]. The inactivation rate of MS2 was enhanced by more than 5 fold depending on the base TiO_2 material, and the inactivation efficiency increased with increasing silver content. The increased production of hydroxyl free radicals was found to be responsible for the enhanced viral inactivation.

Sontakke et al. [14] studied the photocatalytic inactivation of Escherichia coli with combustion synthesized TiO_2 photocatalysts in the presence of visible light. It was found that photolysis alone had a small effect on inactivation while the dark experiment resulted in no inactivation and Ag/TiO_2 showed the maximum inactivation. At a catalyst loading of 0.25 g/L, all the combustion synthesized catalysts showed better inactivation of E. coli compared to commercial Degussa P-25 (DP-25) TiO_2 catalyst. An improved inactivation was observed with increasing lamp intensity and addition of H_2O_2. A negative effect on inactivation was observed by addition of inorganic ions such as $HCO3^-$, SO_4^{2-}, Cl^-, NO_3^-, Na^+, K^+, and Ca^{2+}. The photocatalytic inactivation of E. coli remained unaltered at different pH of the solution.

However, problems such as the instability of the metal-doped titania and relatively low absorption coefficiency of the nonmetal-doped titania in the visible light region, are still unresolved. Thus, exploring the highly-active photocatalysts with narrow band gap, which function in the visible light region, has attracted remarkable attention. Accordingly, the aim of this work was to explore the possibility of the removal of an organic pollutant (phenol) by the application of TiO_2 based photocatalysts. The production of series of metal ions doped or undoped TiO_2 was undertaken by a sol gel method and a wet impregnation method. A standard photoreactor system was designed for such a purpose and the transport/kinetic processes of phenol adsorption and removal were investigated.

2- Materials and Methods

2.1. Preparation of TiO2 based photocatalysts

2.1.1 Sol-gel method

Materials used in this method are shown in Table (1). All the chemicals were laboratory grade. In this method, Titanium (IV) isopropoxide was selected as metal alkoxide precursor because a metal alkoxide with larger molecular weight is relatively stable, which is important in controlling the reaction rate. Isoproponal, 2 (2-ethoxyethoxy) ethanol and ethanol were used as stabilizing agents and solvents for the otherwise immiscible TTIP and H_2O. HCl and H_2SO_4 were used as hydrolysis catalysts, while $CuCl_2$, $CuSO_4$ and $Cu(NO_3)_2$ were employed as dopants.

Undoped and Cu/TiO_2 catalysts were prepared via a sol gel method described by Ding and Liu [15]. Titanium (IV) isopropoxide and alcohol (ethanol, 2(2-ethoxyethoxy) ethanol or isoproponal) were vigorously stirred in a beaker. A mixture of fixed amount of deionsed water (DI water), acid (HCl or H_2SO_4) and alcohol was added drop-wise into the previous TTIP/alcohol solution and magnetically stirred. After gelation, it was dried at 60°C in an oven overnight. The powder was then annealed at a specific temperature for 2 h in furnace. Finally, the catalysts was pulverized through 75μm sieves and kept in a sealed jar for use. For Cu doped TiO_2, a given amount of copper precursor (1 ~ 10 mol % to TiO_2) was mixed with DI water, acid and alcohol solution before the mixture was added into a TTIP/alcohol solution. The rest of the preparation procedure was the same as with undoped TiO_2.

2.1.2 Wet-impregnation method

Materials used in this method are shown in Table (1). The preparation of Cu doped catalysts was via a wet impregnation method described by Di paola et al. [16]. A given type/amount of Copper dopant and TiO_2 P25 were added to 100 mL DI water. The mixture was then magnetically stirred

24 h followed by washing three times using DI water through filtration. Finally, solid was oven dried at 60°C. Further calcination was carried out at 500°C for 2 h.

2.2 Designation of prepared photocatalysts

The denotation of the final catalysts was based on some of synthesis variables, including preparation method, undoped or doped, difference in starting solution composition and annealing temperature. The name of a catalyst can be seen in the format of ATBC. Here "A" stands for the preparation method, it can be sol-gel method (SG) or Wet-impregnation method (IM). "T" is short for TiO_2 and means it is a TiO_2 based photocatalyst. "B" stands for a dopant which could be iron (Fe), Humic acid (HA), Manganese (Mn) but in most cases, it is copper (Cu). "C" stands for different conditions in starting solution composition and annealing temperature, a detailed lists corresponding to this nomenclature can be found in the list of synthesised materials. For example, SGT9 represents a TiO_2 based photocatalyst, which was prepared by the sol-gel method. In the standard sol gel procedure, the starting solution is composed of TTIP, Ethanol, HCl and H_2O at a molar ratio of 1:8:0.06:1. There is no dopant addition in the dried catalysts and the final annealing is at a temperature of 500°C for 2 h. Similarly, SGTCu43 is a TiO_2 based photocatalyst which prepared from sol-gel method. In the standard sol-gel procedure, the starting solution is composed of TTIP, isopropanol, H_2SO_4 and H_2O at a molar ratio of 1:80:0.06:14. It was doped by copper at a level of 0.1 mol% towards TiO_2 and the final annealing conditions are 600°C for 2 h. The system with wet impregnated samples is simpler, they all share a same starting TiO_2 P25 aqueous mixture and therefore, the number 2 in IMTCu2 stands for dopant $CuCl_2$ is introduced at a level of 1.0 mol% before 500°C for 2 h.

2.3 Measurement of photocatalytic activity

2.3.1 Solar box system

The photoreactor consists of two chambers: the lamp and reactor chamber, withthe lamp chamber installed on top of the reactor chamber. Two UVA lamps arelocated in the lamp chamber: (i) a commercial ruptile fluorescent tube lamp and (ii) a fluorescent Blacklight Blue tube lamp (18W, Silva) which transmit ultraviolet radiation peaking at 365 nm. In the reactor chamber, Pyrex glass flasks are employed as batch reactors. Water samples taken from the solar box system at specific time intervals were run at UV-Vis spectrophotometry for phenol degradation experiment.

2.3.2 Continuous flow system

The schematic experimental set up for continuous flow system is shown in Figure (1). It essentially consists of a photocatalytic reactor (PCR) with rectangle cooling jacket. Tap water is circulated in the cooling jacket to control the temperature of PCR at 25ºC (if not otherwise stated). The PCR contains a UV lamp, 1 g/mL photocatalysts and magnetic stirrer. The aqueous liquid running up the reactor was perpendicularly illuminated by immersed UV lamp whose irradiation consistently strikes on the photocatalysts suspension. All parts of this reactor are made from stainless steel in order to enhance the refracted light intensity. Photocatalysts are located inside the inner circle container. Other main components of the system are the control valve, the water grab sampler, a filter, connecting tubes and a water reservoir. The main function of the water tank (WT) is to provide aeration of circulating bacterial suspension. The water grab sampler is made up of water pump and flow meter, which provide the flow of the liquid in the system. To sieve the photocatalyst, a filter has been incorporated downstream of the system. The size of the PCR is around 700 cm^3 and the total volume (V) of water suspension in the system is

controlled at 2000 cm^3 with the flow rate varied from 25 to 125 cm^3 min^{-1}.

2.4 Phenol photodegradation in water

The evaluation of decontamination ability of the prepared catalysts was assessed by photooxidation of phenol in water in the solar box system. To compare the degradation rates between samples, it was ensured that the initial phenol concentration and irradiation intensity were as close as possible. The evolution of the phenol concentration was monitored by UV–vis spectrophotometry at its characteristic 270 nm band, using a centrifuged (4500 r.p.m for 5min) aliquot ca. 2 mL of the suspension. All experiments were carried out in triplicates and DI water was used throughout.

2.5 Characterization and analytical tools

2.5.1 Point of zero charge determination

In the experiment procedure described by Reymond and Kolenda: oxide suspensions with the catalysts solid contents (weight percentage) as 0.01%,0.1%,1%,5%,10% were introduced in glass beakers (capacity:10 mL). The beakers were filled with catalysts oxide suspensions in DI water before sealed in order to minimize the residual air volume above suspension. The beakers were then kept in air and shaken at 200 rpm at room temperature for 24 h. The pH was measured after 24 h of contact time, time for which pH equilibrium was reached in all the cases. It is considered that the PZC value of the oxide is the pH value of the suspension having the higher solid content when pH evolution with solid concentration is low.

235 *2.5.2 Surface area measurement*

236 The sample was pre-treated at 368 K for 1 h and 573K for 3 h under nitrogen, and then a
237 conventional 5-point BET nitrogen isotherm was taken at 77 K. All measurements were carried
238 out on a Micromeretics Gemini analyser. The amount of nitrogen admitted to the catalyst sample
239 was logged and the surface area calculations were carried out by the analyser.

240 *2.5.3 UV-vis spectrophotometer*

241 The concentration of phenol was measured on a double beam spectrophotometer (M350 double
242 beam, Camspec Scientific Intruments Ltd, Sawston, Cambridge, UK). To avoid the imperfection
243 of matching cuvettes when using a double beam, only one beam was used with a 1 cm quartz
244 cuvette. The zero was achieved with DI water and cuvette was regularly left to soak in
245 concentrated hydrochloric acid. The spectra of absorption of the phenol indicates the existence of
246 an absorption band corresponding to the transition n- ~ n * to a wavelength of 270 nm. The
247 indicated absorbance is proportional to the concentration in phenol, according to the law of Beer
248 Lambert in the studied concentration domain 0 - 100 mg/l.

249

250 **3- Results and Discussion**

251 *3.1 Preliminary results*

252 Preliminary tests were undertaken to check the viability of the solar box as a light input system.
253 A series of doped TiO_2 were prepared using the standard sol gel method as detailed in section
254 2.1.1 and a brief summary is provided in Table (2). The length of experiment was extended to 24
255 h in order to set a proper sampling time interval for later experiments. A typical trail time would
256 be set at around 10 h with 2 h sampling intervals. Blank samples were introduced using
257 irradiated phenol without the addition of photocatalysts.

As shown in Figure (2), the prepared dopant-free TiO_2 photocatalyst was very effective in the reaction of phenol decomposition, and a linear dependence of phenol concentration versus time was obtained. An analogous linear dependence was also observed for other doped TiO_2. From these, consistent data were obtained using the Cu doped TiO_2, therefore, this was selected for further investigations. On the other hand, humic acid doped TiO_2 and Mn doped TiO_2 (1 mol% dopant: Ti^{4+}) are almost photochemically inactive and low photoreactivity for phenol degradation is observed for Fe^{3+} doped TiO_2.

The effect of individual metal ions on the photocatalytic activity of metal ion doped TiO_2 is a complex area. An interpretation of reactivity order is difficult since it is probably the net result of a combination of factors such as surface area, crystallinity, crystal size, band-gap energy etc. Moreover, the addition of metals could be either beneficial or detrimental depending on whether such metals decrease the rate of electron-hole recombination or act as electron-hole recombination centers [17].

Using phenol as target organic pollutant and catalysts prepared from sol gel method, a significant photoacitivity decrease in metal ion doped TiO_2 compared with dopant free TiO_2 was also reported in literature [18] with the dopant ions behaving as recombination centres of the photoproduced charge carriers. The presence of dopant at a concentration level of 1 mol% seems to be adequate to produce a negative influence by decreasing the density of surface-active centers. However, it is still too early to conclude that doping is negative for the photodegradation reactions. Dominant parameters such as character and concentration of the dopant, preparation method and reaction regimes could be the key to tune up the reactivity of doped TiO_2.

3.2 The effect of initial phenol concentration

The photodegradation efficiency of phenol is related closely to its initial concentration. Higher phenol concentrations lead to a decrease in the degree of degradation within the same time period. The main reactions occur on the surface of the solid photocatalyst and at a high initial concentration all catalytic sites are occupied. Further increase in the concentration can provide excess reactant and also limits the adsorption of reaction intermediate on the reactive surface. This prohibits the penetration of light reaching the surface and consequently less HO· is formed resulting in a decrease of the observed zero-order rate constant.

The effect of the initial concentration of phenol is presented in Figures (3a) and (3b), and Table (3). An increase in the initial phenol concentration substantially decreases in the degradation rate. The remarkable inhibitory effect of the initial concentration of phenol on the apparent rate constant has been reported with the photocatalytic decomposition of phenol following a negative first order reaction kinetics [19,20]. However, there is no clear understanding of this negative influence of initial phenol concentration. It has been proposed [21] that the phenoxide ions ArO^-, which are generated from the dissociation of phenol, maybe compete with and replace the adsorbed OH^- on the limited number of reactive positions on the surface of catalysts. Then the generation of OH• will be reduced since there are fewer active sites for the generation of OH• radicals. It is also worth noting that Phenol is always adsorbed on the TiO_2 surface in a phenoxide ion [22].

At a concentration of 20 mg/L, there seems to be sufficient reactant molecules for the reactive sites, however, a further increase in the concentration may prohibit the penetration of light. Meanwhile, an excess phenol concentration increases the concentration of reaction intimidates to be treated, which in turn also compete with the phenol for the reactive sites on the TiO_2 surface.

In the photomineralization of organic pollutants sensitized by TiO2, it has been traditionally reported that the initial rate of disappearance of the pollutant fits a Langmuir–Hinshelwood (L–H) kinetic scheme [23]. The Langmuir-Hinshelwood (L-H) kinetic model assumes rapid, reversible adsorption of a reactant on the catalyst surface prior to reaction. The L-H rate equation is of the form:

$$r_o = -\frac{d[C]}{dt} = \frac{k.K[C]}{1+K[C]} \quad (1)$$

Where: r_o is the initial rate of disappearance of the organic substrate; k is a rate constant for the reaction (mmol L^{-1} min^{-1}), reflecting the limiting rate of reaction at maximum coverage under the given experimental conditions; K is the constant for adsorption of the organic substrate onto the TiO_2 surface (L $mmol^{-1}$); and C is the concentration of the organic substrate (mmol L^{-1}) in solution.

The above equation can be inverted to solve for k and K.

$$\frac{1}{r_o} = \frac{1}{K} + \frac{1}{k.K[C]} \quad (2)$$

The slope and intercept from a plot of $1/r_0$ versus 1/[C] can be used to determine k and K.

Phenol oxidation data for both undoped and Cu doped TiO_2 at pH 5 were plotted using Equation (2) with reasonably good fits ($R^2 > 0.95$). The rate constant and the binding constant for TiO_2 catalyst are -0.16×10^{-3} mmol L^{-1} min^{-1} and -17.57 L $mmol^{-1}$, respectively, while for Cu/TiO_2 they are -0.5×10^{-4} mmol L^{-1} min^{-1} and -15.67 L $mmol^{-1}$, respectively. Traditionally, k is taken to represent the Langmuir absorption constant of the species (organic substrate) on the surface of TiO_2, and K is a proportionality constant which provides a measure of the intrinsic reactivity of the photoactivated surface with organic substrate [23]. The L-H rate constants at pH = 6.3

derived from Equation (2) for both catalysts showed the same order of reactivity, but the undoped TiO_2 is almost 3 times more active than Cu doped TiO_2. However, it is generally assumed that both rate constants and orders are only "apparent". They serve to describe the rate of degradation, and may be used for reactor optimization, but they have no physical meaning, and may not be used to identify surface processes.

3.3 The effect of catalyst dose

To increase the performance of heterogeneous photocatalytic process, one common way is to increase the contact area of TiO_2 along the light path. The amount of catalyst used is also related to cost effectiveness. A low mass of catalyst requires an extension of light exposure and hydraulic retention time which increases the cost effectiveness. On the other hand, an excessive amount of catalyst has cost implications and potential to reduce photoactivity due to increased turbidity of the suspension. Hence, it is important to find the optimal amount catalyst mass for the system.

To study the influence of catalyst mass, the quantity of catalyst was varied whilst keeping the concentration of phenol solution equal to 50 mg/L. Figures (4a) and (4b) illustrated the influence of catalyst mass on the degradation of phenol, in the range from 0.1 g/L to 2 g/L. It is illustrated that phenol concentration decreases monotonically with an increase in catalyst mass in the water. It is obvious that the higher catalyst mass, the higher the area of the reactive surface available for adsorption and reaction will be. But the effect of catalysts dose cannot be indefinitely beneficial. Above a certain level, the degradation rate will remain constant even with increased catalysts loading. This rule is more obvious with TiO_2 in Table (4). As the concentration of the catalyst increases, the amount of adsorbed photons as well as phenol molecules increases with respect to the number of catalysts molecules. The concentration in the area of illumination also increases

and thus the reaction rate is enhanced. All studies of photocatalysis note the existence of an optimal concentration of TiO_2. It can be concluded that a suitable amount of TiO_2 for the photocatalytic reaction is approximately 1-3 g/L depending on types of reactor and TiO_2 powders [19, 21]. In our experiment, the catalyst loading is approximately 1.5 g/L for undoped TiO_2, while it can be in excess of 2 g/L for Cu doped TiO_2. Previous researchers suggest [24] that high-TiO_2 dose might lead to aggregation of the catalyst particles accompanied by reduction in reactive sites. Furthermore, shielding effects may occur due to high turbidity along with high concentration of catalyst which prevents light penetration. A consequent rate decrease is always a possibility if the dose is increased above a certain limit and hence the catalyst concentration must be monitored to ensure efficient photodegradation.

3.4 The effect of solution pH

Industrial effluents may be basic or acidic and therefore the effect of pH should be investigated. The pH value of phenol solution has a significant influence on the photocatalytic process for a variety of reasons, including the TiO_2 surface charge state, the flat-band potential, and the dissociation of phenol. These processes all are strongly pH dependent. The relative concentration of functional groups on the surface of hydrated TiO_2 ($TiOH_2^+$, TiOH and TiO^-) varies depending on the pH, due to surface hydroxyl groups gaining or losing a proton.

$$\gg Ti(OH)_2^+ \overset{pKa1}{\longleftrightarrow} \gg TiOH + H^+ \quad (3)$$

$$\gg TiOH \overset{pKa2}{\longleftrightarrow} \gg TiO^- + H^+ \quad (4)$$

For Degussa P25 TiO2, pKa1= 4.5 and pKa2 = 8. The pH of the point of zero charge, pH_{pzc}, can be calculated from half of the sum of pKa1 and pKa2: $pH_{pzc} = 6.25$. The surface of TiO_2 shows a net positive charge as pH decrease below the pH_{pzc} and the negative charged surface dominates

as pH increases above pH_{pzc}. Phenol (pK_a= 9.95) exists as a molecular form in a neutral and weakly basic solutions. High pH value favours the dissociation of phenol into phenoxide ion $C_6H_5O^-$. As illustrated in Figure (5), a decrease in pH decreases the degradation rate. There is less discrepancy between the neutral and basic environment, as compared to acidic conditions, which may be explained by the surface chemistry of the system. At a low pH = 3.3 the molecule of phenol is non-dissociated (neutral) and the surface of TiO_2 is either at a neutral state (TiOH) [24] or positively charged as suggested by Al-Ekabi et al. [25]. These researchers studied the photocatalytic oxidation of chlorinated phenol solutions and observed that the protonation of the TiO_2 surface at low pH might be responsible for the inhibition of TiO_2-mediated adsorption of chlorinated hydrocarbon. In this study, as the pH is adjusted with HCl, the Cl^- anions are also adsorbed at the surface of TiO_2. There is competition between the adsorption of the anions and phenol, hence the generation of OH· radicals is retarded. In the case of substances which are weakly acidic, the photocatalytic degradation of phenol increases at lower pH because of an increase in adsorption. At pH= 6.3, which is near its theoretical isoelectric point, the surface of TiO_2 is negatively charged while the phenol adsorption is at its maximum and the quantity of Cl^- ions is lower [24]. Meanwhile, when the pH increases, the active hydroxyl groups on the TiO_2 surface increase accordingly. Consequently, a faster generation of OH· radicals accelerates the phenol oxidation [21]. It is also consistent with the work of O'Shea and Cardona [26], who found that the initial reaction rates for phenol degradation steadily increases in the pH range from 3.0 to 9.0, however a lack of significant acceleration in the initial reaction rates was found at higher pH. Similarly in our experiment, there is no significant difference in the initial reaction rate at a pH of 10.3. This can be attributed to the fact that phenol is entirely dissociated into phenoxide ion, which will compete for the reactive sites with the –OH groups and reduce the OH· radicals.

Meanwhile, there is a phenomenon of repulsion between the negatively charged surface of TiO_2 and phenoxide ions, which explains the decrease in the rate of phenol oxidation. Although the pH dependence phenomena have been observed by many authors, detailed explanations are still not conclusive. Okamoto et al. [27] studied the photocatalytic oxidation of a 1 mM phenol solution with TiO_2 and suggested that the optimum pH value was 3.5. Augugliaro et al. [19] found that the kinetic rate increased as the pH value increased to about 3, and then it decreased steadily until a pH value of about 12.5, beyond which the reaction rate constant again sharply increased. Some other investigators have reported no effect of pH on the rate of phenol removal.

3.5 The effect of light intensity

Since the TiO_2 powder is suspended in a stirred solution, the light intensity will affect the degree of light absorption by the TiO_2 surface [21]. Previous investigators have also studied the light-intensity effect on the phenol degradation [27]. There are two ways of varying the light source intensity in our solar box system. One is to change the distance of light and batch reactor. Another is simply changing the light input sources, comparing UVA light with natural sunlight.

3.5.1 Comparison between dark and irradiation

In our batch reactor system, the catalyst used in this experiment is TiO_2 P25. Control is achieved by exposing phenol in the solar box system, while another flask containing phenol and the same amount of TiO_2 is kept in the dark during the same experiment period.

It is evident in Figure (6) that the presence of both catalyst and irradiation act favourably in the photocatalytic process. In the absence of TiO_2 P25, phenol can hardly be degraded during a time period over 20 h. Similar trends can be observed for the absence of irradiation, which also suggests that TiO_2 powder cannot promote the oxidation of phenol [21] and that the adsorption

of phenol is negligible in the dark. The decline of phenol in the presence of TiO_2 along with UVA irradiation may be attributed to the photooxidation process rather than adsorption.

3.5.2 Comparison between the position of flask container

In our batch reactor system, 100 mL quartz flasks are employed as the container which can be placed either in position "A" that is just next to the lamp assuming the distance to be 0 cm or position "B" that has a distance of 10 cm from the lamp. It is clear from Figure (7) that the nearer the flask is to the lamp, the more efficient the photodegradation of phenol in the solar box. The obvious explanation is that in the position "A", the same size flask received more irradiation than the flask in position "B". Hence, it suggests that in the design of reactor system, effort can be made to reduce the space between the reactor and the lamp.

3.5.3 Comparison between artificial UVA and sunlight

The threshold wavelength corresponds to the band gap energy for the semiconductor catalyst, e.g., for the TiO_2 catalyst having band gap energy of 3.02 eV, the ideal wavelength is 400 nm. Sunlight therefore is a valid source of irradiation for the excitation of the catalyst and has a considerable economic advantage. A direct comparison between the results with solar box system and sunlight from a clear sky is shown in Figure (8). The control shows no sign of phenol degradation under sunlight. In the presence of TiO_2, the concentration of phenol drops to around 10 mg/l in 5 hours, indicating 80% degradation. By comparing the sunlight and the solar box, it can be seen that the former is almost 4 times more efficient than the latter. Similarly, it has been reported [28] that the time required for 90% degradation of the phenol in sunlight in the presence of 0.1% TiO_2 suspension was 55 min, approximately 1.7 times less than with the 100 W medium

pressure mercury lamp. The results confirmed the possibility of substitute UV irradiation with direct sunlight. At the same time, data obtained in the solar box system can be extrapolated from the laboratory set-up to a larger scale with reasonable confidence.

3.6 The effect of catalysts preparation method

The properties of catalysts are very much dependant on the preparation methods, therefore, two different preparation methods for doped TiO_2 were used as specified in Table (5). As depicted in Figure (9), IMTCu2 exhibits a better efficiency than SGTCu17 in phenol degradation, both of which are prepared from $CuCl_2$ at a same concentration. The different in preparation methods determine the dopant concentration distribution in the TiO_2 lattice structure, which may explain the variation in photoactivity. In the wet impregnation method, the dopants may be confined to the surface and/or to a few top layers of TiO_2 particles as dispersed species due to the moderate calcination temperatures. The dopants in the sol gel methods are homogenously "dissolved" in the TiO_2, although further calcinations may change their concentration distribution, the sol gel method may produce a more homogenous doped catalyst, which is not always favoured.

Conclusions:

In the solar box system with two 18W UVA lamps, undoped TiO_2 and Cu doped TiO_2 showed considerable phenol degradation. The efficiency of photocatalytic reaction largely depends on the photocatalysts and the methods of preparation the photocatalysts. The doping of Fe, Mn, and humic acid at 1.0 M% via sol gel methods were detrimental for phenol degradation. The unremarkable inhibitory effect of initial phenol concentration on initial phenol degradation rate reveals that photocatalytic decomposition of phenol follows pseudo zero order reaction kinetics. A concentration of at least 1 g/L TiO_2 and Cu doped TiO_2 is required for the effective degradation of 50 mg/L of phenol at neutral pH. It was found that pH plays a major role in the phenomena of adsorption of phenol onto TiO_2. The increase in OH^- concentrations at a higher pH values is beneficial of phenol degradation. However, the competition between phenoxide ion, Cl^- and OH^- for the limited number of reactive sites on TiO_2 will be a negative factor in the generation of hydroxyl radical. TiO_2 is not active in the dark and the adsorption is negligible. The dependence of phenol degradation rate on the light intensity was investigated, with the results implying that direct sunlight can be a substitute for UV lamps, and that photocatalytic treatment of organic pollutants may be an efficient technique.

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Name	Chemical Formula	Manufacturer	Description
Sol-gel method			
Titanium (IV) isopropoxide(TTIP)	$Ti(OC_4H_9)_4$	Acros Organic, UK	metal alkoxides precursor
Anhydrous isoproponal	$(CH_3)_2CHOH$	Acros Organic, UK	alcohol solvent
Anhydrous 2(2-ethoxyethoxy) ethanol	$CH_3CH_2OCH_2CH_2O$-CH_2CH_2OH	Acros Organic, UK	alcohol solvent
Anhydrous ethanol	CH_3CH_2OH	BDH chemicals, UK	alcohol solvent
37% Hydrochloric Acid	HCl	Fisher Chemicals, UK	hydrolysis catalyst
Sulphuric acid	H_2SO_4	BDH chemicals, UK	hydrolysis catalyst
Anhydrous copper (II) chloride	$CuCl_2$	Acros Organic, UK	dopant
Anhydrous cupric sulphate	$CuSO_4$	BDH chemicals, UK	dopant
Anhydrous copper (II) nitrate	$Cu(NO_3)_2$	Fisher Chemicals, UK	dopant
Anhydrous Manganese chloride	$MnCl_2$	Fisher Chemicals, UK	dopant
Iron(II) chloride	$FeCl_3$	Fisher Chemicals, UK	dopant
Humic acid	n/a	Acros Organic, UK	dopant
Wet-impregnation method			
Anhydrous copper (II) chloride	$CuCl_2$	Acros Organic, UK	dopant
Anhydrous cupric sulphate	$CuSO_4$	BDH chemicals, UK	dopant
Titania P25	TiO_2	DegussaCo. Germany	80% anatase, 20% rutile; BET area: 50 m^2g^{-1}

575 **Table 1:** Materials used in sol-gel method.
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Table 2: Summary of photocatalysts used in preliminary experiment.

Material	Sample	Treatment
Cu doped TiO_2 from sol gel method	SGTCu17	Hydrolysis and condensation of sol mixture (TTIP: Ethanol: HCl: H_2O: $CuCl_2$ = 1:8:0.3:1: 0.01) at room temperature and followed by drying at 500 ºC for 2 h
Mn Doped TiO_2 from sol gel method	SGTMn1	Hydrolysis and condensation of sol mixture (TTIP: Ethanol: HCl: H_2O:$MnCl_2$=1:8:0.3: 1:0.01) at room temperature and followed by drying at 500 ºC for 2 h
Iron doped TiO_2 from sol gel method	SGTFe1	Hydrolysis and condensation of sol mixture (TTIP: Ethanol: HCl: H_2O:$FeCl_3$=1:8:0.3: 1:0.01) at room temperature and followed by drying at 500 ºC for 2 h
Humic acid doped TiO_2 from sol gel method	SGTHA1	Hydrolysis and condensation of sol mixture (TTIP: Ethanol: HCl: H_2O: humic acid=1:8:0.3:1:0.01) at room temperature and followed by drying at 120 ºC for 2 h
Undoped TiO_2 from sol gel method	SGT5	Hydrolysis and condensation of sol mixture (TTIP: Ethanol: HCl: H_2O=1:8:0.3:1) at room temperature and followed by drying at 500 ºC for 2 h

Table 3: The initial phenol concentration effect on phenol disappearance rate on TiO_2 (Sample SGT5) and Cu doped TiO_2 (Sample SGTCu17) suspension from different initial concentration: 10 mg/L, 20 mg/L, 50 mg/L and 100 mg/L. Container size= 100 mL, Catalyst dose = 1g/L, pH = 6.3, Temp = 25°C.

phenol $1/[C_o]$, (L mol^{-1})	TiO_2 ($1/r_0$) (L min $mmol^{-1}$)	Cu- TiO_2 ($1/r_0$) (L min $mmol^{-1}$)
940	-1.681×10^4	-5.908×10^3
1880	-1.573×10^4	-5.048×10^3
4700	-1.147×10^4	-3.518×10^3
9400	-6.123×10^3	-2.874×10^3

Table 4: Rate constants and binding constants from Langmuir-Hinshelwood plots for phenol disappearance on TiO_2 (Sample SGT5) and Cu doped TiO_2 (Sample SGTCu17) suspension from different initial concentration: 10 mg/L, 20 mg/L, 50 mg/L and 100 mg/L. Container size = 100 mL, Catalysts dose = 1g/L, pH = 6.3, Temp = 25°C.

Catalysts	**Rate constant *k*** **(mmol L^{-1} min^{-1})**	**Binding constant K** **(L $mmol^{-1}$)**
TiO_2	-0.16×10^{-3}	-17.57
Cu/TiO_2	-0.50×10^{-4}	-15.67

Table 5: The catalyst dose effect on phenol disappearance rate on TiO_2 (Sample SGT5) and Cu doped TiO_2 (Sample SGTCu17) suspension in different catalysts dose: 0.1, 0.5, 1.0, 1.5 and 2.0 g/L. Container size = 100 mL, initial phenol concentration = 50 mg/L, pH = 6.3, Temp = 25°C.

Catalyst ($g\ L^{-1}$)	**TiO_2 r_0** ($g\ h^{-1}\ L^{-1}$)	**Cu doped TiO_2 r_0** ($g\ h^{-1}\ L^{-1}$)
0.1	-0.00197	-4.94×10^{-5}
0.5	-0.00248	-4.15×10^{-4}
1.0	-0.00298	-8.95×10^{-4}
1.5	-0.00334	-9.85×10^{-4}
2.0	-0.00338	-11.8×10^{-4}

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726 **Table 6:** Photocatalysts used in studying the effect of catalyst's preparation method.
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Material	Sample	Treatment
Cu doped TiO_2 from sol-gel method	SGTCu17	Hydrolysis and condensation of sol mixture (TTIP: Ethanol: HCl: H_2O: $CuCl_2$ = 1:8:0.3:1:0.01) at room temperature and followed by drying at 500 ºC for 2 h
Cu doped TiO_2 from wet-impregnation method	IMTCu2	Magnetic stirring of aqueous mixture of $CuCl_2$ and TiO_2 P25 (molar ratio: 0.01) at room temperature for 24 h and followed by filtration, oven drying at 60 ºC overnight and 500 ºC for 2 h

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Figure Captions:

Figure 1: Schematic layout of continuous flow system.

Figure 2: Phenol disappearance on TiO_2 (Sample SGT8) and doped TiO_2 suspension. Container size = 25mL, Catalysts dose = 1g/L, initial phenol concentration = 50 mg/L, pH = 6.3, Temp = 25°C.

Figure 3: Zero order plots of phenol disappearance on **(a)** TiO_2 (Sample SGT5) and **(b)** Cu doped TiO_2 (Sample SGTCu17) suspension from different initial concentration: 10mg/L, 20mg/L, 50mg/L and 100mg/L. Container size = 100mL. Catalysts dose = 1g/L, pH = 6.3, T = 25°C.

Figure 4: Phenol disappearance on **(a)** TiO_2 (Sample SGT5) and **(b)** Cu doped TiO_2 (Sample SGTCu17) suspension in different catalysts dose: 0.1, 0.5, 1.0, 1.5 and 2.0 g/L. Container size = 100 mL, initial phenol concentration = 50 mg/L, pH = 6.3, T = 25°C.

Figure 5: Phenol disappearance from TiO_2 (Sample SGT5) suspension at different pH: 3.3, 6.3 and 10.3. Catalysts dose = 1g/L, initial phenol concentration = 50 mg/L, container size = 100 mL, T = 25°C.

Figure 6: Phenol disappearance on TiO_2 (Sample p25) suspension in different irradiation conditions: Dark and solar box system UVA irradiation. Container size = 100 mL, Catalysts dose = 1g/L, initial phenol concentration = 40 mg/L, pH = 6.3, T = 25°C. Control is used with absence of TiO_2 in solar box system.

Figure 7: Phenol disappearance on TiO_2 (Sample P25) suspension in at different distance from lamp: A is 0 cm and B is 10 cm. Container size = 100 mL, Catalysts dose = 1g/L, initial phenol concentration = 40 mg/L, pH = 6.3, T = 25°C.

Figure 8: Phenol disappearance on TiO_2 (Sample SGT5) suspension in different irradiation conditions: Direct sunlight and solar box system UVA irradiation. Container size = 100 mL, Catalysts dose = 1g/L, initial phenol concentration = 50 mg/L, pH = 6.3. Control is used with absence of TiO_2 in direct sunlight.

Figure 9: Phenol disappearance on Cu doped TiO_2 using sample prepared from different method sol gel (Sample SGTCu17) and wet-impreganation (Sample IMTCu2) in solar box system UVA. Container size = 100 mL, Catalysts dose = 1g/L, initial phenol concentration = 50 mg/L, pH = 6.3. Control is used with absence of Cu-TiO_2 in the same solar box system.

776 **Figure 1**
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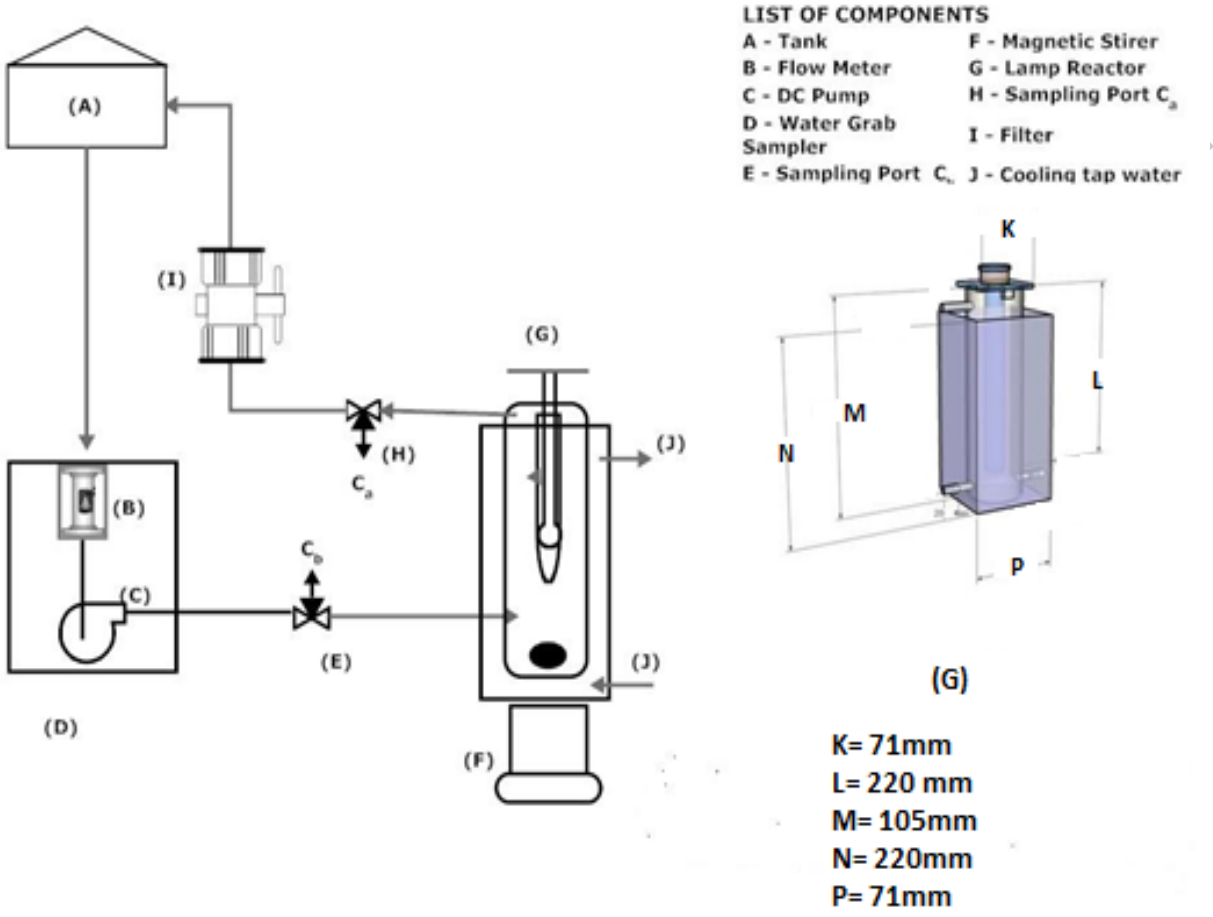

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796 **Figure 2**
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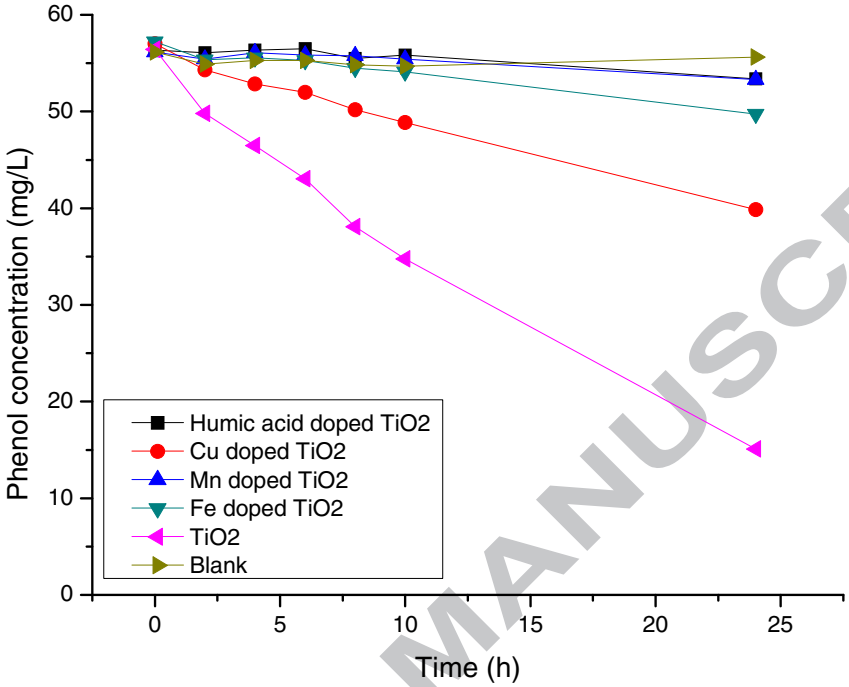

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813 **Figure 3**

814 **(a)**

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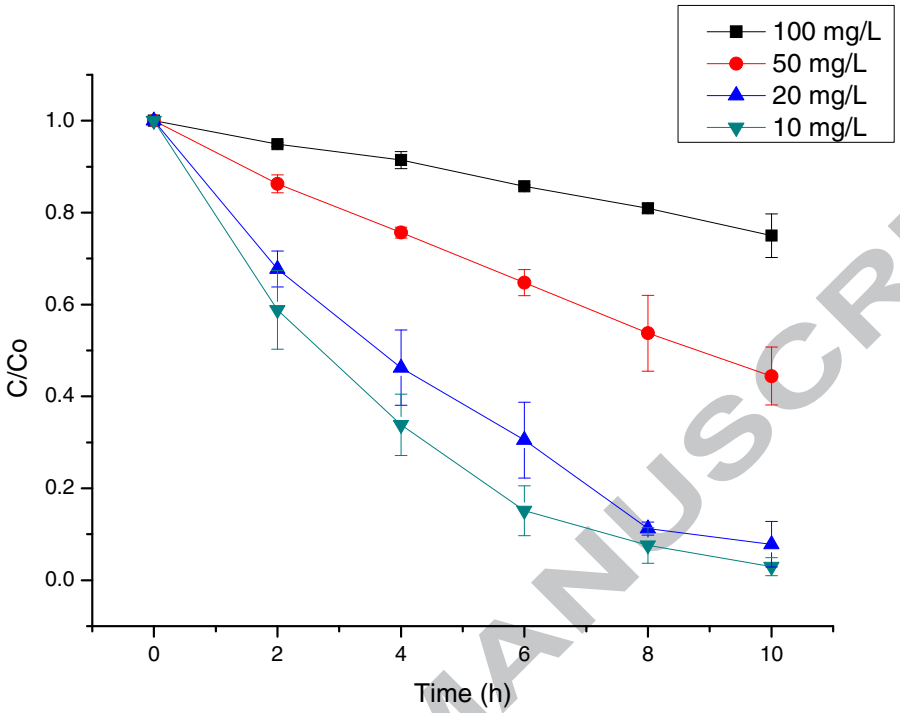

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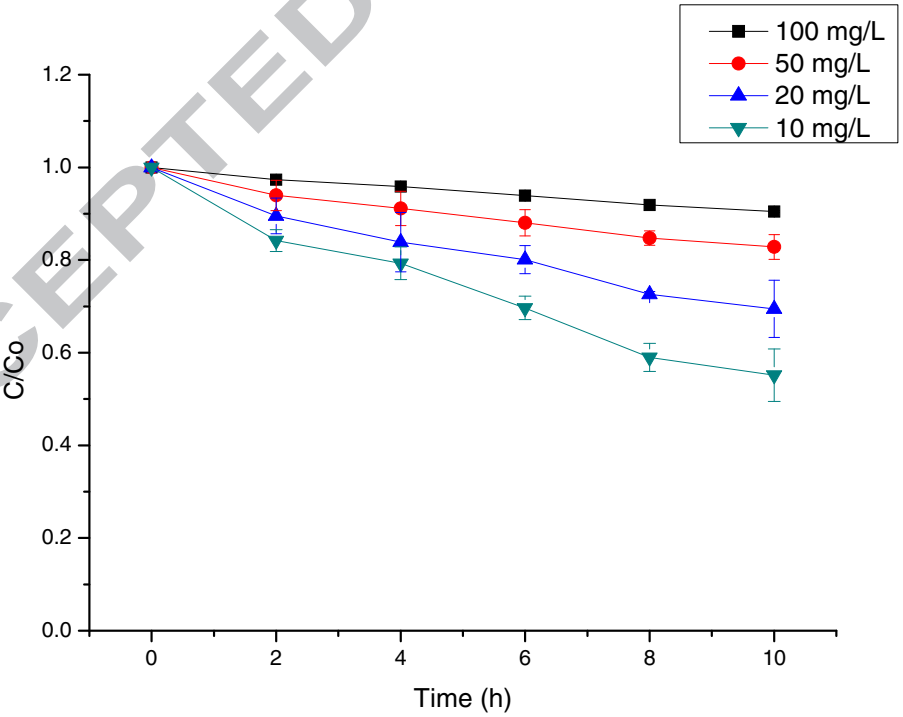
817 **(b)**



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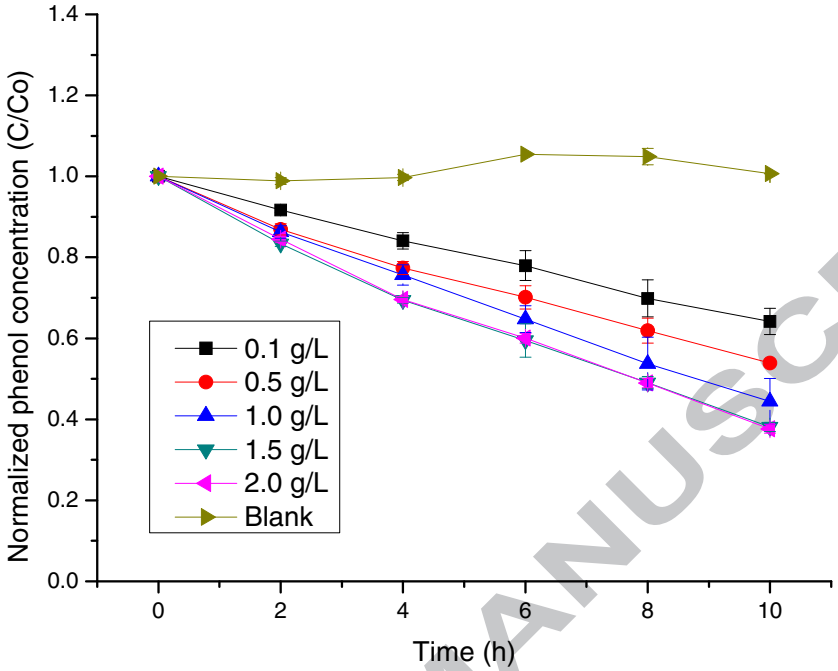
819 **Figure 4**

820 **(a)**



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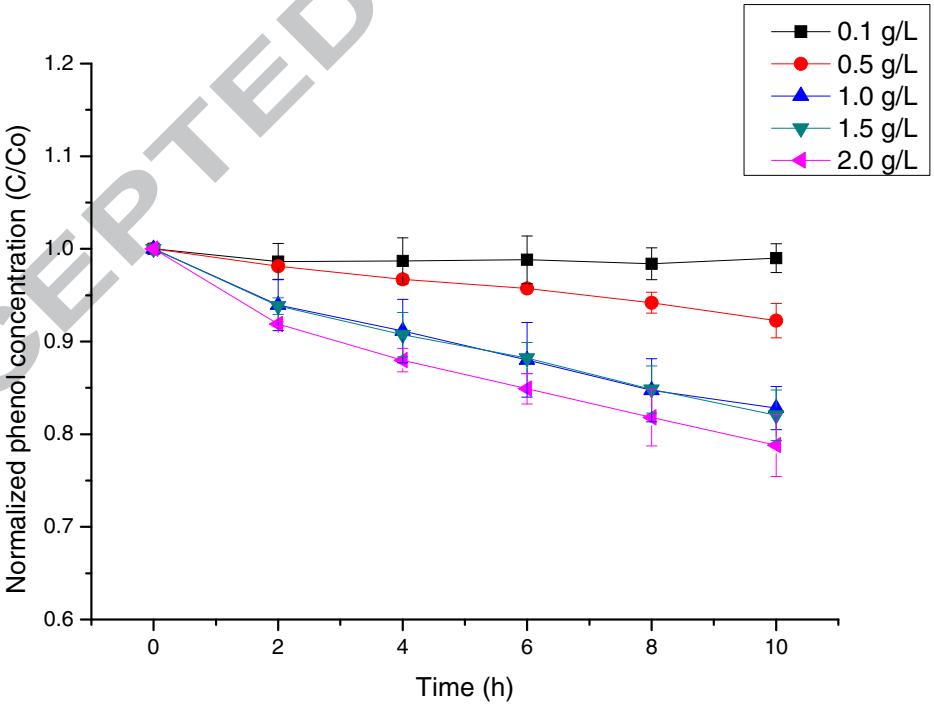

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824 **Figure 5**

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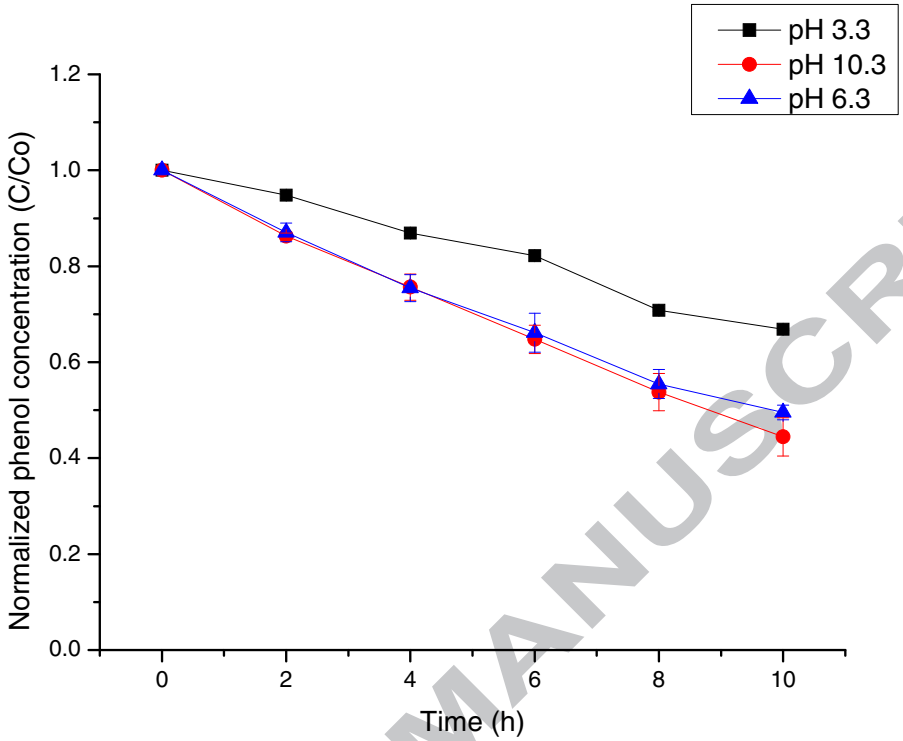

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847 **Figure 6**

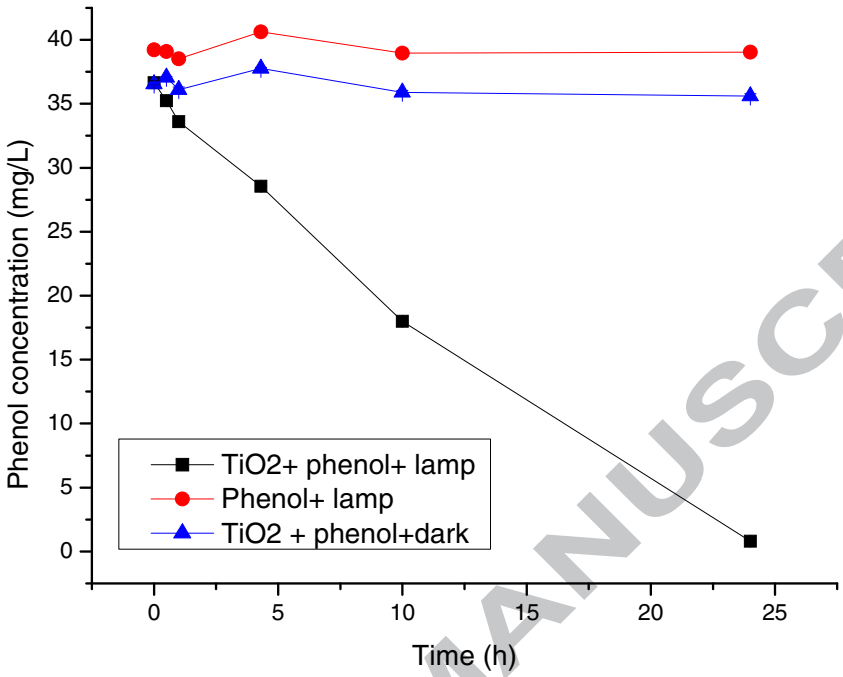

Figure 7

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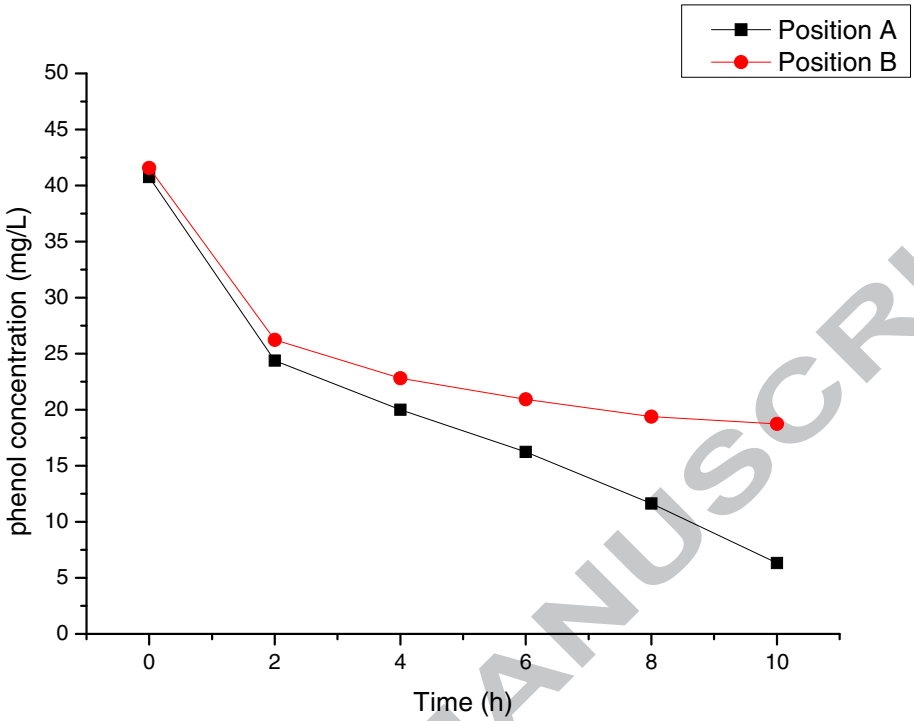

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898 **Figure 8**

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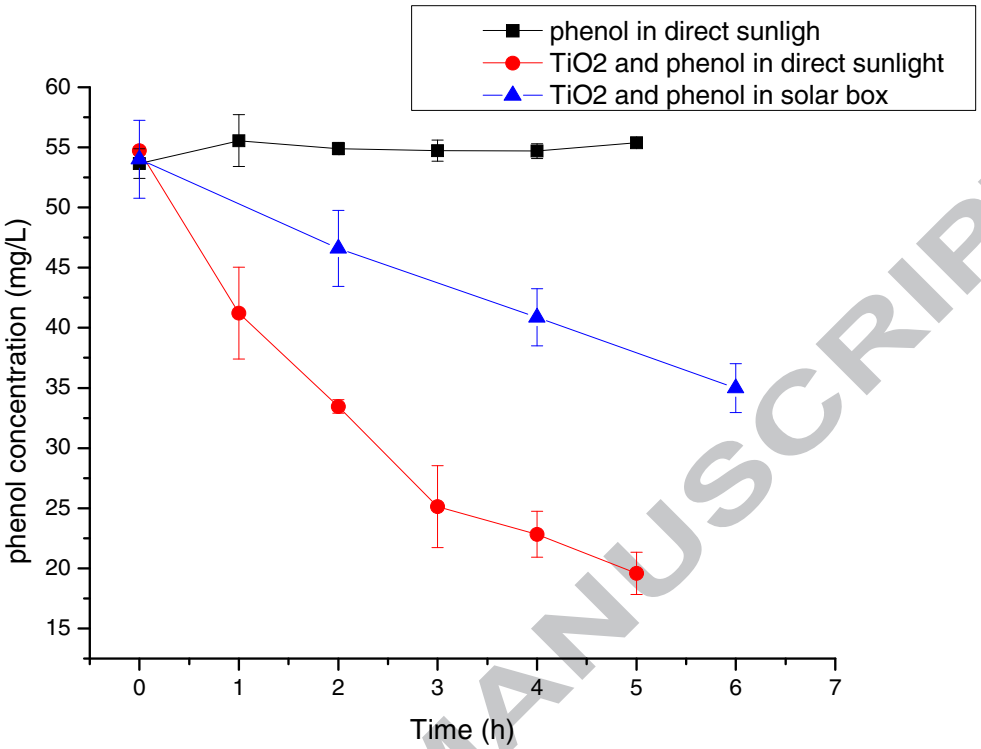

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923 **Figure 9**

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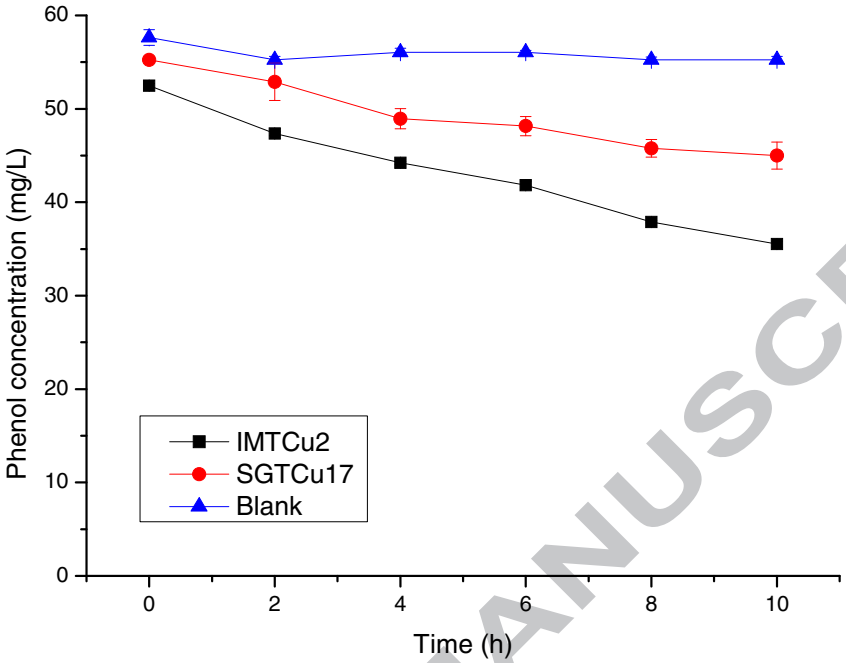

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939 **Research Highlights:**

940 **1-** Removal of phenol by the application of TiO_2 based photocatalysts was explored.

941 **2-** Undoped TiO_2 and Cu doped TiO_2 showed considerable phenol degradation.

942 **3-** The efficiency of photocatalytic reaction depends on the methods of preparation.

943 **4-** Photocatalytic decomposition of phenol follows pseudo zero order reaction kinetics.

944 **5-** Direct sunlight can be a substitute for the UV lamps.

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