



Photocatalytic discoloration of aqueous phenol red solutions using TiO₂ nanocatalyst

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Abstract

In this paper, photocatalytic degradation of Phenol Red (PR) was evaluated in a slurry batch reactor using nano TiO₂ (Degussa P-25) as a catalyst. The effect of the variation of different parameters, such as catalyst loading, initial PR concentration, inorganic salts and type of light sources on the rate of photocatalytic degradation was also studied, and the optimum conditions for the maximum degradation rate were determined. The photocatalytic degradation process was well described by pseudo-first order reaction. The optimum TiO₂ loading, which provides enough surface area for reaction without irradiation loss due to scattering of UV light, was found to be 0.5 g/L, and PR concentration was 50ppm. Furthermore, the effects of inorganic salts were investigated. Result showed that photocatalytic degradation rate was affected significantly in the presence of nitrate and chloride.

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Introduction

Water is one of the fundamental requirements of life and any undesired addition of chemical substances lead to its contamination and unfit for human use. Generally, various dyes found in industrial effluents, ultimately enter the aquatic ecosystem and can create various environmental hazards (Lachheb *et al.*, 2002). These may have adverse, sometimes irreversible effects on animals and plants, as well. There are many traditional wastewater treatment methods such as adsorption, flocculation and many others which are ineffective on every pollutant. Besides, those treatment methods may not completely neutralize toxic contaminants but instead leaving hazardous substance as residues (Forgacs *et al.*, 2004; Senthilkumar *et al.*, 2006). However, one way to destroy pollutants without generating secondary toxic materials is photocatalysis.

Heterogeneous photocatalysis is an advanced oxidation process (AOP) that can be successfully used to oxidize many organic pollutants present in aqueous systems (Bizani *et al.*, 2006; HajdSalah *et al.*, 2004). Among the semiconductors used, TiO₂ is considered particularly efficient (Colon *et al.*, 2008; Wang *et al.*, 2007) owing to the formation of an electron-hole pair under illumination with near UV light (Senthilkumar *et al.*, 2006). Especially the TiO₂/UV system, due to its non-toxic, inexpensive, and high reactive nature, has been mainly used to oxidize wastewater-containing dyes (Wu *et al.*, 2008; Tang *et al.*, 1995). Many studies have shown the effects of operational parameters of the conducted photocatalytic processes on the quality and quickness of degradation of organic compounds (Kuo *et al.*, 2001; Tan *et al.*, 2011). Lakshmi *et al.* showed during their studies that the rate of photocatalytic reaction increased with a rise of the amount of catalyst, and remained almost constant above a certain level, then decreased. In this study, this special feature of TiO₂ nanomaterial photocatalyst was exploited on the decomposition of organic dye like PR (Fig.1). Phenol Red possesses wide range of applications, such as bromination catalysts, pH indicator, estrogenic properties and

screening test (Wong *et al.*, 2006; Mitsuhashi *et al.*, 2003). The most important physicochemical properties of PR are presented in Table 1. Despite its wide range of applications, little is known on the photocatalytic degradation properties of the TiO₂ nanoparticles on this material. Therefore, present study was aimed at elucidating the effect of different processing parameters, such as concentration of organic PR, photocatalyst loading, inorganic salt, and light sources on the degradation of this harmful material.

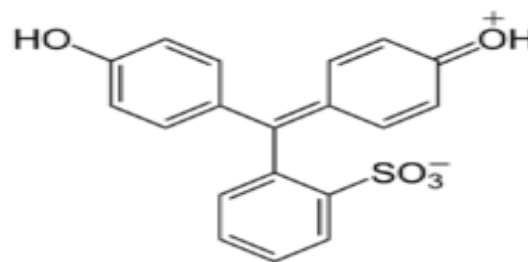


Fig. 1. Molecular structure of PR.

Table 1. some physicochemical properties of Phenol Red (PR).

Properties	value
Common Synonyms	Phenolsulphonphthalein
Commercial name	Phenol Red
Molecular formula	C ₁₉ H ₁₄ O ₅ S
Molecular Weight	354.38
Absorption maxima	435-440 nm
Solubility in water	0.77g/l
pK _a	8.8
Colour	Liquid Yellow to red

Materials and methods

Reagents

Titanium dioxide P-25 (Degussa) was used as a catalyst. This product contains 80% anatase and 20% rutile, and has a specific surface area of 50 m² g⁻¹ and a particle size of 21 nm. Dye, Phenol red was used as model organic compound for photocatalytic tests. Other chemicals were purchased from Merck (Darmstadt, Germany) with a purity of >99% and deionized laboratory water was used for making

aqueous mixtures. Initial pH of the solution was adjusted by using 0.1N NaOH and 0.1N HCL.

Procedures

The photocatalytic degradation was carried out in a 1000mL cylindrical stainless steel reactor (9 cm ID×25 cm H) with three UV-C (F6T5/GL 6W, low pressure Hg lamp close to monochromatic output at 254 nm, Philips, Poland) lamps. The UV light sources were surrounded by a Quartz glass tube to preventing direct contact with solution. Suspensions of the photocatalyst and aqueous contaminant solutions were kept aerated and stirred by a steady stream of air to improve contact between dye molecules and TiO₂ particles and maintain homogeneity.

Table 2. Effect of initial concentration on the photocatalytic degradation of PR.

Initial conc. (ppm)	k(min⁻¹)	R²
5	0.0879	0.981
10	0.0611	0.996
20	0.0418	0.990

Photocatalytic Analysis

The photocatalytic experiments were conducted to investigate the photodegradation of the PR in aqueous suspension system. After the UV light irradiation for a certain time interval, each sample was centrifuged to separate the suspensions of the TiO₂ nanoparticles. The residual PR concentration in the solution was analyzed by a UV-Vis Spectrophotometer (JENWAY 6305 UV/Vis model) at 440 nm. A 5 mL aliquot was collected after 0, 5, 15, 30, 60, 90 and 120 min of reaction time.

Results and discussion

Kinetics of phenol red disappearance

Aqueous solution of PR in the presence or absence of TiO₂ was irradiated by three UV-lamps. The role of photocatalytic degradation and the effect of direct photolysis on the decomposition of PR were studied.

In Fig. 2, the removal efficiency of PR is plotted as a function of reaction time. A control experiment was performed by an identical aqueous solution without catalyst. The result reveals that the degradation of PR follows pseudo first-order kinetics with respect to the PR concentration, i.e.

$$-\frac{dc_t}{dt} = K_{ap} C_t \tag{1}$$

The integration of Eq. (1) with the boundary condition that at the start of irradiation ($t = 0$), the concentration is the initial one, $C_t = C_0$, yields Eq. (2):

$$-Ln\left(\frac{C}{C_0}\right) = K_{ap} t \tag{2}$$

Where, k_{ap} (min⁻¹) is the apparent first order rate constant, C_t is the concentration of PR at time t (min) and C_0 is the initial concentration of PR. Kinetic studies were assessed by monitoring the PR concentration at certain interval of time. The slope of the plot gave the value of k_{ap} .

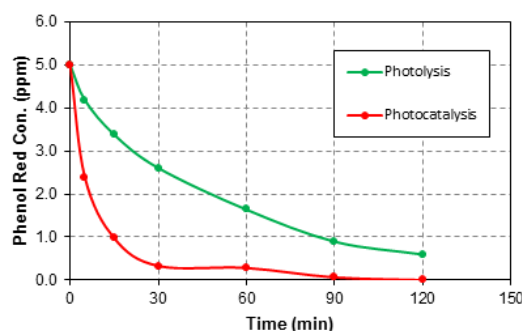


Fig. 2. Variation of PR concentrations versus irradiation time without and with the photocatalysis.

The resulting first order rate constants have been used to calculate degradation rate for PR and were used for comparison of the efficiency of photocatalytic process under different experimental conditions.

Effect of PR concentration

The effect of initial concentration of PR on the photodegradation in the range of 5-20ppm is demonstrated in Fig. 3 and table.3. It reveals that with increase in the concentration of PR, the degradation rate increases up to a certain limit. Further increase in concentration of PR led to decrease in the degradation rate after concentration is

attributed the fact that light absorbed by the PR is more than that of TiO₂. Thus light absorbed by the PR is not effective to carry out the degradation. Further, the equilibrium adsorption of PR on the catalyst surface active site increases and more and more molecules of PR get adsorbed on the surface of the catalyst. Therefore, competitive adsorption of OH⁻ on the same site decreases and consequently the amount of ·OH and O₂⁻ on the surface of catalyst decreases. For all initial PR concentrations, the catalyst, irradiation time and intensity of light were constant. Since the generation of ·OH does not increase, the probability of phenol molecules to react with ·OH decreases, therefore, a decrease in the degradation efficiency is observed. Similar results have been presented for the photocatalytic oxidation of other organic compounds (Farzadnia *et al.*,2014).

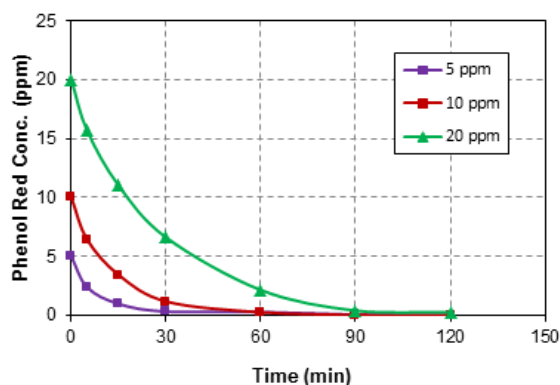


Fig. 3. The effect of initial PR concentration on the photodegradation rate (T = 25 °C, and C_{cat}= 0.5 g L⁻¹).

Effect of photocatalyst loading

The amount of TiO₂ in the solution is an important parameter that can affect the photodegradation rate of PR. It is found that the degradation value increases with the catalyst loading, but to a certain concentration. The concentration of the catalyst loading was varied from 0.1 to 1.0 to study the effect on the photodegradation of the PR. The photodegradation efficiency of PR for different concentration of TiO₂ was shown in Figure 4. This experiment was carried out under the UV light. The values of the pseudo-first-order apparent kinetic constant for several initial catalyst concentrations are

presented in Table 3. In Figure 4, the percentage of degradation generally increases as the concentration of the TiO₂ catalyst was increased. With the increased of the catalyst concentration, the number of active sides on the photocatalyst surface increases, which in turn, increase the number of hydroxyl, and superoxide radicals. However, when the concentration of TiO₂ catalyst increases above certain value, the degradation rate seems to reach equilibrium value and decreases slightly (Qamar *et al.*, 2006; Chen *et al.*, 2007). The equilibrium value is reach due to the concentration of PR while the decrease is probably due to the photon interception of the light rays by the suspension. Similar results have been reported for degradation of methamidophos (Wei *et al.*, 2009) and dimethoate (Chen *et al.*, 2007).

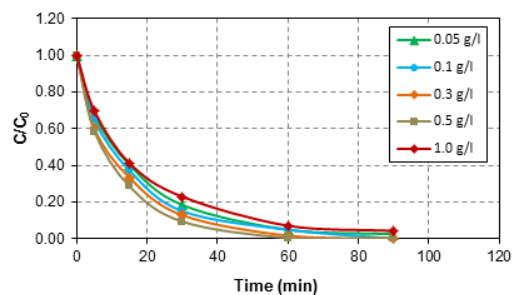


Fig. 4. Effect of TiO₂ loading on the photocatalytic degradation of PR (T = 25 °C, C₀= 5 ppm).

Table 3. The pseudo-firstorder reaction rate constants for the photocatalytic degradation of PR at various catalysts loading.

Catalyst Loading	K_{ap}	R²
0.05 g/l	0.0497	0.994
0.1 g/l	0.0499	0.982
0.3 g/l	0.0674	0.998
0.5 g/l	0.0928	0.991
1.0 g/l	0.0431	0.991

Effect of inorganic anions

Wastewater commonly contains significant amounts of inorganic anions, and these anions have serious effect on water properties. The anions can change the

ionic strength of the solution, therefore, affect the catalytic activity and hence the photocatalytic degradation (Calza and Pelizzetti, 2001). The effect of chloride, nitrate, and sulfate was investigated using corresponding Na⁺ as cationic. These anions could be adsorbed on the surface of TiO₂ in acidic condition by electrostatic attraction. The values of the pseudo-first-order apparent kinetic constant for several inorganic salt are presented in Table 4. Figure 5 illustrates the effect of these anions on photocatalytic degradation of PR. All anions were found to inhibit photocatalysis, with the order Of SO₄²⁻>NO₃⁻>Cl⁻. This can be explained on the basis of reaction of h_νB⁺ and ·OH with anions which behave as scavengers, and thus inhibit the degradation. In conclusion, the adsorbed anions compete with organic contaminants for the photo-oxidizing species on the surface of catalyst and prevent the photocatalytic degradation of the phenol (Chen *et al.*, 2007).

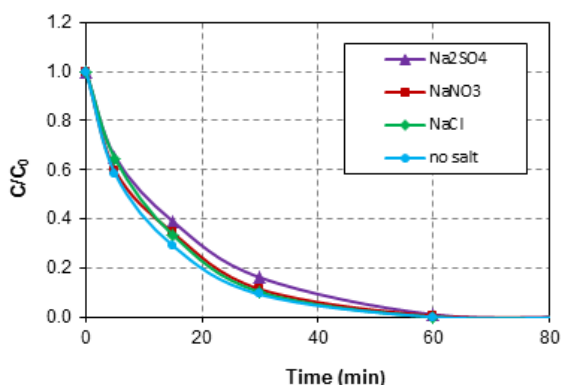


Fig. 5. Effect of inorganic anions additions on the photocatalytic degradation of PR (T = 25 °C, Co= 5 ppm, and Ccat= 0.5 g L-1).

Table 4. Pseudo-first order rate constant for the degradation of PR.

Parameters	k(min ⁻¹)	R ²
NaCl	0.0751	0.998
NaNO ₃	0.0704	0.993
Na ₂ SO ₄	0.0592	0.995
No Salt	0.0777	0.996

Effect of UV light radiation

Another parameter that could influence degradation rate of the dyes is the wavelength of the UV light irradiating the TiO₂ particles. Therefore we used two UV light wavelengths (254 nm and 365 nm, both 18W) to degrade PR (keeping other conditions constant). The effect of different light sources on the photocatalytic degradation rate is shown in Fig.6. UVC lamp as a light source resulted in the highest apparent rate constant (k_{ap}=0.087 min⁻¹) that may be due to the highest illumination intensity. It means that the activity of the photocatalyst depends strongly on the light-illumination (energy per unit area) or the photon flux on the surface of the photocatalyst. The order of degradation rate using different light sources was shown to be UV-C>UV-A. This may be explained by an increase in the number of photons striking per unit area as the light intensity was increased (Savitri *et al.*, 2008).

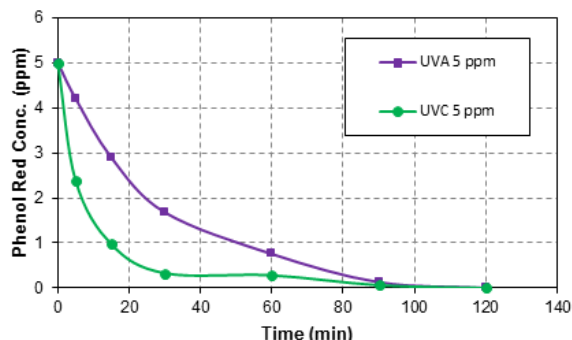


Fig. 6. The effect of light sources on the photocatalytic degradation of PR (T = 25 °C, Co= 5 ppm, and Ccat= 0.5 g L-1).

Conclusions

In this study, we investigated the degradation of Phenol Red as the model pollutant of water by TiO₂ dispersion under irradiation with UV light. Treatment of dyes has been carried out by varying the parameters like PR initial concentration, catalyst loading, inorganic salt and light intensity. The degradation process follows pseudo first-order degradation behavior. Experimental results indicate that the decolorization of dye is effective in the presence of catalyst. Increasing TiO₂ concentration beyond 0.5 g/L showed a reduction on the

photodegradation of PR due to light shielding effect. The removal efficiency and the constant rate of degradation increased with decreasing initial concentration of PR. The optimum range of PR concentration was 5ppm. The inhibition effect of anions on degradation of PR was in the order $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$. The order of degradation rate using different light sources was shown to be UV-C > UV-A.

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