



Oxidation of aqueous organic pollutants in industrial waste water by heterogeneous photocatalysis using a cocurrent downflow bubble column contactor (CDC)

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Abstract

The heterogeneous photocatalytic oxidation of aqueous organic pollutants to innocuous products (i.e. CO₂, H₂O) has been studied in a novel pilot scale photocatalytic reactor. Phenol was used as a representative organic pollutant and TiO₂ as a photocatalyst in aqueous dispersions under UV irradiation. Complete degradation of phenol (100 %) was achieved in about 190 min of irradiation for an initial organic substrate loading of 100 mg/dm³ and 18 dm³ solution. The reaction was strongly pH dependent with pH 2.5-3.0 producing the maximum reaction rates. Results also indicated that complete mineralization of substrate and intermediates could not be accomplished without the addition of small quantities of H₂O₂. A Langmuir-Hinshelwood type rate expression and a pseudo 1st-order equation were used to model the reaction rate and kinetics. The experiments exemplified the suitability of the CDC photocatalytic reactor as an alternative device to degrade aqueous organic pollutants.

1. Introduction

As the world population has been predicted to steadily escalate into the year 2000 [1], the search to develop innovative and more efficient waste water treatment technologies to sustain and improve water quality is of paramount importance. Furthermore, the abatement of toxic discharges into large bodies of water will require a serious and unified effort from all sectors of the community (i.e. government, industrial, domestic and scientific) in order to preserve the global environment. This paper reports on research which has been conducted in a novel pilot scale reactor with the objective of taking the heterogeneous photocatalytic oxidation of aqueous organic pollutants to the industrial level.

The photocatalytic degradation of aqueous pollutants in suspensions of TiO₂ semiconductor photocatalyst and Ultra-Violet (UV) irradiation has been a subject of considerable interest over the past 10-15 years (Herrmann *et al.* [2]).

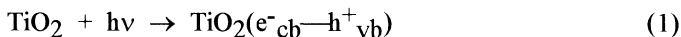


Many experiments have been conducted; e.g. Okamoto *et al.* [3,4], Serpone *et al.* [5], Augugliaro *et al.* [6] with all these studies showing very promising results, however, these investigations were performed on the small laboratory scale *ca.* 0.5-2 dm³. More recently, work has been reported (Ollis & Al-Ekabi [7]) of research underway to take this technology a step further to the pilot and subsequent industrial level. Our research has been motivated to investigate the performance of the CDC contactor as an alternative device to oxidize aqueous organic pollutants by heterogeneous photocatalysis.

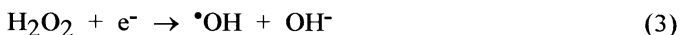
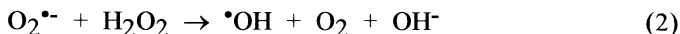
1.1 Generalized Theory

There have been a number of excellent contributions (Okamoto *et al.* [3,4]; Serpone *et al.* [5]; Augugliaro *et al.* [6]; Bard [8]) devoted to establishing the theoretical criteria for the oxidation of aqueous organic compounds with irradiated semiconductor materials (e.g. TiO₂).

In simple terms, the irradiation of a photocatalyst by light of a suitable wavelength and energy ($h\nu$) induces a separation between the electrons (e^-) and holes (h^+) in the valence band (vb) and migration of these electrons to the conduction band (cb). Thus for TiO₂:



The subsequent migration of these species to the particle surface promotes oxidation (holes) and reduction (electrons) reactions *in situ*. It has been accepted (Serpone *et al.* [5]) that hydroxyl radicals $\cdot\text{OH}$ are the chief oxidizing species acting on the organic compounds and may be produced by the reaction of free surface electrons in combination with generated or added oxidants (e.g. O₂, H₂O₂):



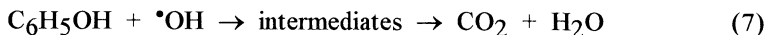
Simultaneously, $\cdot\text{OH}$ may be produced by the reaction of holes (h^+) with other species:



In addition to the above reactions, $\cdot\text{OH}$ can be formed by the reaction of H₂O₂ and UV irradiation alone (Serpone *et al.* [5]):



Taking all the above reactions into consideration, the complete degradation of an organic species (eg. Phenol) with $\cdot\text{OH}$ may be summarized as follows (Augugliaro *et al.* [9]):



Some of the typical intermediate products formed in reaction (7) may be hydroquinone and catechol which must further undergo oxidation. Okamoto *et al.* [3] have postulated the reaction pathways for their degradation.

2. The CDC Photocatalytic Reactor

The CDC is a novel gas-liquid contactor which has been studied in detail as a chemical reactor for slurry and fixed bed catalytic hydrogenation [10] and gas absorption unit (Sulidis *et al.* [11]). Further development and modification has yielded the CDC photocatalytic reactor (Sulidis [12]; Boyes *et al.* [13]). Figure 1 depicts the basic design features of the reactor prototype.

The reactor comprises of two independent operating units. The top section is a gas-liquid mixing zone with a metal cap affixed at the apex. An orifice of set diameter is attached to the underside of the cap. Gas (oxidant) and liquid (aqueous pollutant and suspended catalyst) streams combine in a 'T' configuration and enter co-currently through the orifice into a fully flooded column. Within this region, high rates of mass transfer between the gas and liquid phase is attained due to the energy and turbulence imparted by the high velocity gas-liquid jet. This section is also characterized by close approach to equilibrium of the gas and liquid phase (~97 %). The bottom section of the reactor comprises the photocatalytic reaction zone which centrally houses a UV lamp.

2.1 Experimental Rig

This research was undertaken using two QVF glass CDC photocatalytic reactors of 6.18 dm³ (reactor A) and 1.83 dm³ (reactor B) reaction zone volume respectively. These reactors were operated in batch mode with recycle. A flow sheet of the complete reactor circuit (reactor A) is illustrated in figure 2 and was of similar configuration for each reactor. Table 1 displays the principal operating parameters used in the experiments. For the large reactor, the total volume of solution was maintained at about 18 dm³. The irradiation was supplied by a 30 W UV tube. The irradiation (reaction) time was considered to be the total residence time of a fluid element in the reaction zone and was evaluated by an equation of the form:

$$t_r = \frac{V_r}{V_s} \times t_0 \quad (8)$$

The reactor operating temperature, approximately 50 °C, was maintained from the heat supplied by the recirculation pump.

Table 1. Reactor Operating Conditions

Parameter	Reactor A	Reactor B
Reaction Zone Volume	6.18 dm ³	1.83 dm ³
Orifice Diameter	0.005 m	0.005 m
Recirculation Rate	10 dm ³ /min	5 dm ³ /min
Reactor Circuit Volume	17 - 18 dm ³	7 dm ³
Oxygen Flowrate	0 - 0.05 dm ³ /min	0 - 0.1 dm ³ /min
Reactor Temperature	318-323K	318-323K
Reactor Pressure	1.0 barg	1.0 barg
Lamp Rating	1 x 30W UV @ 254 nm	2 x 8W UV @ 315-400 nm
Photon Flux	1.06 x 10 ⁻⁶ einstein/s	4.47 x 10 ⁻⁷ einstein/s



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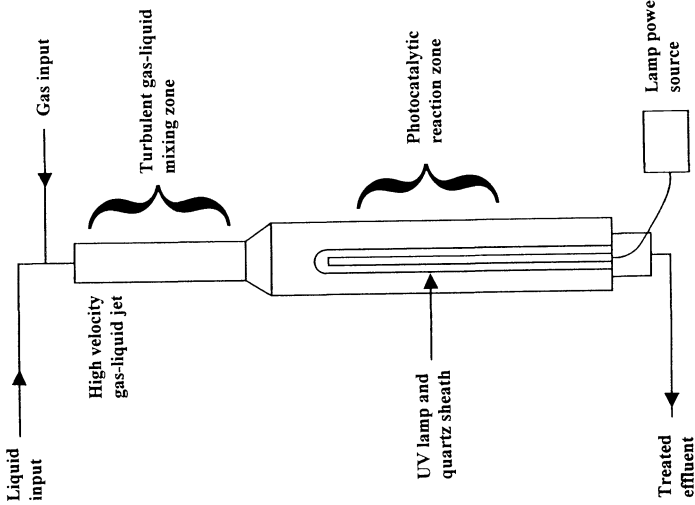


Figure 1. Basic design principle of the CDC photocatalytic reactor.

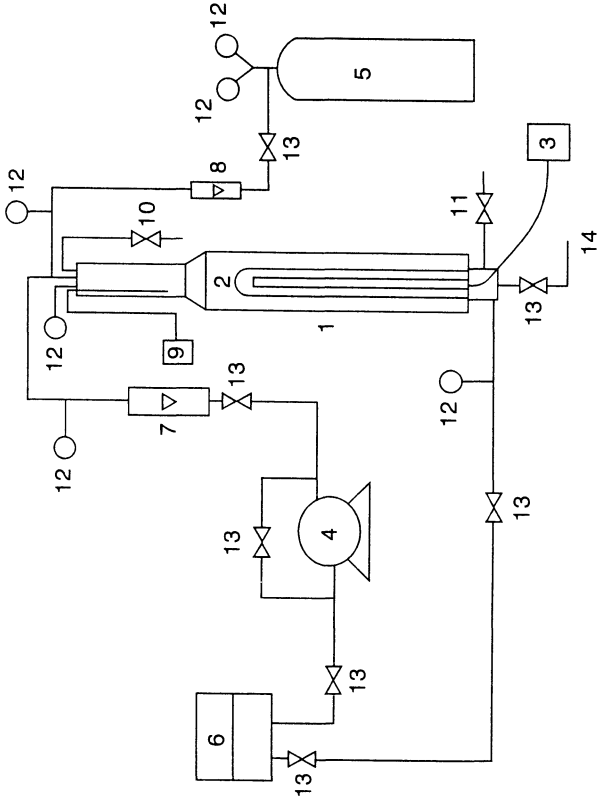


Figure 2. Diagrammatic flowsheet of the experimental set-up for reactor A.

- 1. CDC photocatalytic reactor; 2. UV tube & quartz sheathings; 3. Lamp power supply; 4. Recirculation pump; 5. Gas cylinder; 6. Reservoir; 7. Liquid rotameter; 8. Gas rotameter; 9. Thermocouple & temperature meter; 10. Reactor purge; 11. Pressure relief valve; 12. Pressure gauge; 13. Valve; 14. Sample point

2.2 Experimental Procedure

This research was conducted using Degussa P25 TiO₂ as the photocatalyst and was used as received. A P25 loading of 0.03 % w/w (0.3 g/dm³) was used for reactor A and 0.2 % w/w (2 g/dm³) for reactor B as these concentrations were found to achieve the best oxidation rates. The majority of experiments were undertaken using an initial phenol concentration of 100 mg/dm³. Reactor A was operated continuously for up to 9 hours which corresponded to about 190 min of reaction (irradiation) time. The solution pH was adjusted using H₂SO₄ and NaOH. Samples of the reactor effluent (*ca.* 20 cm³) were taken at either 30 min or 60 min intervals and were filtered with glass microfibre paper.

Phenol concentration and total organic carbon (TOC) were determined colorimetrically using a conventional method [12]. In addition, phenol and intermediate products were analyzed by HPLC (Waters 490E) equipped with a Nova-Pak C₁₈ 3.9mm x 15cm column. The mobile phase was 50 % methanol/water run in isocratic mode. Other experiments were conducted to observe the effect of dispersion additives (i.e. H₂O₂) and doped (i.e. transition metals, noble metals, porphyrins) TiO₂ on reaction rate. A detailed description of all experimental procedures may be found in other reports (Sulidis [12]; Boyes *et al.* [13]).

3. Results and Discussion

Some experiments were focused on modelling the phenol oxidation rate and kinetics. A pseudo 1st-order rate constant k_1 was obtained from the equation proposed by Okamoto *et al.* [3]:

$$\ln(C/C_0) = -k_1 t \quad (9)$$

Moreover, the reaction rate was found to fit a Langmuir-Hinshelwood kinetic equation of the type (Herrmann *et al.*[2]):

$$r = \frac{k K C}{1 + K C} \quad (10)$$

The constants in equation (9) and (10) are determined from a least-squares analysis of experimental data. Table 2 and 3 display some of the constants evaluated from the study. The results [12,13] have indicated that these expressions are applicable to the CDC reactor, however they may suffer the disadvantage of being limited solely to the reactor and operating conditions used to validate the models.

Table 2. Langmuir-Hinshelwood Kinetic Parameters for CDC Reactors

Reactor	Solution pH	Rate Constant k (mol /dm ³ min)	Adsorption Constant K (dm ³ / mol)
Reactor A	5.5	1.034 x 10 ⁻⁵	1065.44
Reactor B	7.0	2.045 x 10 ⁻⁴	73.15

Operating Conditions: Reactor A, 0.03 % w/w P25, O₂ flowrate 0.05 dm³/min; Reactor B, 0.2 % w/w P25, O₂ flowrate 0.05 dm³/min



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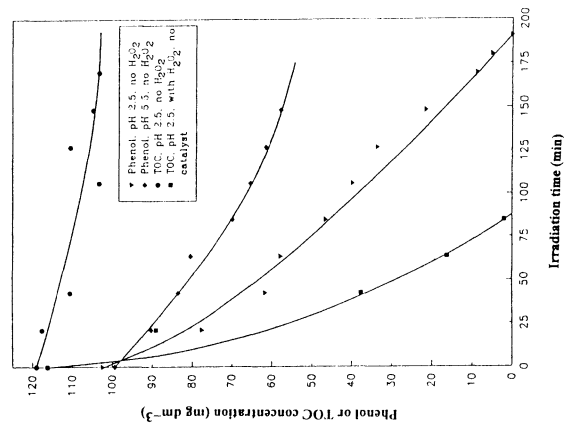


Figure 3. Phenol or TOC concentration as a function of irradiation time for reactor A.
 Operating Conditions: Initial phenol 100 mg dm⁻³, 0.03 % w/w P25, O₂ flowrate 0.05 dm³ min⁻¹, 0.02 dm³ 28 % w/v H₂O₂ each hour

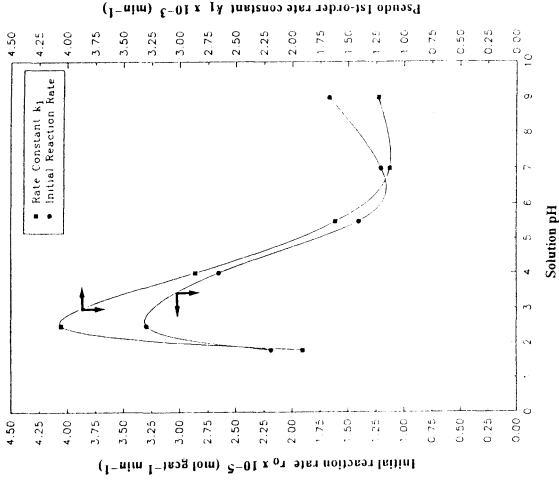


Figure 4. Effect of solution pH on reaction and kinetic parameters.
 Operating Conditions: Reactor A, Initial phenol 100 mg dm⁻³, 0.03 % w/w P25, O₂ flowrate 0.05 dm³ min⁻¹

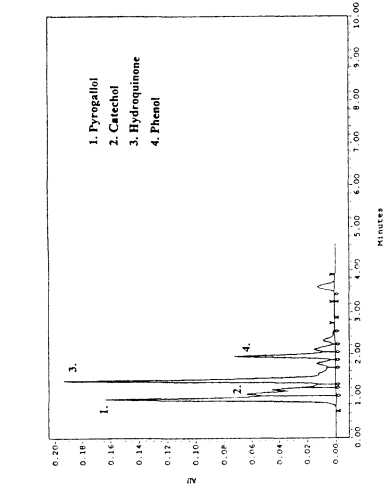


Figure 5. Typical HPLC chromatogram
 Operating Conditions: Reactor A, Initial phenol 100 mg dm⁻³, 0.03 % w/w P25, O₂ flowrate 0.05 dm³ min⁻¹, pH 2.5, irradiation time 150 min

Table 3. Some Reaction and Kinetic Characteristics for CDC Reactors

Reactor	Solution pH	Initial Reaction Rate r_0 (mol /gcat min)	Pseudo 1st-order rate constant k_1 (/min)
Reactor A	5.5	1.403×10^{-5}	1.611×10^{-3}
Reactor A	2.5	3.297×10^{-5}	4.054×10^{-3}
Reactor B	7.0	2.504×10^{-5}	6.816×10^{-3}

Operating Conditions: Initial phenol concentration 100 mg/dm^3 ; Reactor A, 0.03 % w/w P25, O_2 flowrate $0.05 \text{ dm}^3/\text{min}$; Reactor B, 0.2 % w/w P25, O_2 flowrate $0.05 \text{ dm}^3/\text{min}$

Figure 3 illustrates phenol and TOC concentration as a function of irradiation time. The results exhibit a similar relationship *viz*; phenol and TOC oxidation proceeds monotonically with reaction time. Total phenol (100%) degradation is achieved in about 190 min of irradiation at pH 2.5. At the higher pH 5.5, the reaction rate decreases (see Table 3; Reactor A). The results demonstrate that without the addition of small quantities of H_2O_2 (*ca.* 20 cm^3 intermittently each hour) the organic intermediates cannot be completely oxidized under the conditions studied. Our results [12,13] have confirmed that the performance of the CDC reactor and phenol oxidation is better without photocatalyst present *viz*; with H_2O_2 and UV irradiation alone.

Figure 4 displays the effect of solution pH on reaction rate and 1st-order rate constant. As shown, maximum reaction rate lies in the region pH 2.5-3.0 confirming other published reports [3]. Figure 5 shows a HPLC chromatogram of an effluent sample from reactor A after 7 hours ($t_r=150 \text{ min}$) of continuous operation. As can be seen, hydroquinone, catechol and pyrogallol are the major intermediates present which is in agreement with the literature reports [3,5,6].

The results [12,13] have also shown that no enhancement in reaction rate can be achieved with the use of transition metal, noble metal and porphyrin doped TiO_2 when compared with TiO_2 alone. All dopants were found to retard the oxidation rate in the CDC reactor at the conditions studied.

4. Conclusion

This study has demonstrated the applicability of the CDC photocatalytic reactor to degrade aqueous organic pollutants. It is of our opinion, that further detailed studies on the pilot scale should be performed, to ascertain whether the use of TiO_2 photocatalyst and UV irradiation alone is feasible for industrial scale-up of the process. Our experiments have shown that $\text{H}_2\text{O}_2/\text{UV}$ irradiation alone is a better combination than TiO_2/UV irradiation to promote the oxidation of aqueous organic pollutants as this may be due to the presence of larger concentrations of $\cdot\text{OH}$ radicals in the presence of H_2O_2 . Further studies will involve more powerful UV sources and extending the O_2 mass transfer zone over the full length of the reactor.



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Symbols

C	Organic concentration	mol/dm ³
C ₀	Initial organic concentration	mol/dm ³
K	Adsorption constant	dm ³ /mol
k	Rate constant	mol/dm ³ min
k ₁	Apparent 1st-order rate constant	/min
r	Oxidation rate	mol/dm ³ min
t ₀	Reactor operating time	min
t _r , t	Reaction (irradiation) time	min
V _S	Total volume of reactor system	dm ³
V _r	Reaction zone volume	dm ³

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