

Analysis of Recycled-Glass Immobilised and Suspended TiO₂ in the Photocatalytic Oxidation of Chlorophenols in Batch Processes

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Abstract. The photocatalytic oxidations of multi-substituted chlorophenols were studied in mixed-reactor batch systems. Glass supported immobilised titanium dioxide photocatalysis was investigated for degradation efficiency in comparison to photolysis. The project aim was to determine preliminary effectiveness of advanced oxidation process principles in a theoretically non-optimised installation, by applying low cost materials to counter the principal recovery shortfall of suspended catalyst in photocatalytic applications. Titanium dioxide catalyst mounting onto glass units was achieved through furnace heating of a thin-film coating layer. Kinetic profiles were determined for singular compound transformations. The overall performance of the immobilised catalyst data set recorded promising findings and showed significant efficiency in treatment of higher level chloride-substituted phenols by registering near complete oxidation.

Keywords: Photocatalysis, semiconductor, chlorophenols, immobilisation

1. Introduction

Photocatalysis is an advanced oxidation process (AOP) technique that degrades organic classes of compounds at near ambient conditions [1]-[3], complete mineralisation can be achieved in conducive installations [4]-[7]. Advanced treatment technologies are increasingly employed in dealing with environmentally persistence pollutants due to the inability of conventional water treatment processes in removing new and emerging pollutants. Commercialisation of photocatalysis has suffered stagnation due to known and accepted scientific draw-backs such as the inability to reclaim the semiconductor catalyst in suspended slurry-type applications, and the energy intense irradiation in the ultra-violet region of the spectrum required to excite electrons from the semiconductor surface sites to facilitate reduction and oxidation pathways [8]-[10]. Semiconductor catalyst-immobilisation is one of the solutions for the catalyst reclamation problem. A study by Pozzo et al. [11] proposed various catalyst-immobilised support material, and formulated a support material criteria, that suggested that the support material be transparent to UV radiation, to have strong surface chemical-physical adherence with catalyst particles without impeding reactivity, to offer a high specific surface area, and good adsorption capability. Advantages of immobilised catalyst applications that have been documented including improved surface area, superior adsorption properties [12]-[14] and reduced charge recombination [15]. Immobilisation of semiconductor can be achieved on a variety of support material such as pellet substrates, soft materials and on rigid substrates [16]. This study will focus on rigid and thick support material, this type of catalyst fixing has been successfully achieved in studies by Zhuang et al. [17] and Pelentridou et al. [18]. Immobilised photocatalysts do have short-falls that are mainly related to their inferiority to liquid-solid interfaces of suspended applications listed in studies by Nasalevich et al. [19] 2014 and Pozzo et al. [11]. Due to the complexity of the photocatalytic process and the multiplicity of variables involved, there is no question on the superiority and theoretical efficiency of suspended oxide catalyst in comparison to immobilised catalyst, there however is a need for a

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feasibility assessment on the potential effectiveness of large-size low cost support material and potential applications. This study will evaluate the feasibility of immobilising photocatalyst on large-size adhesive material of silica glass. Immobilising of titanium dioxide will be attempted on recycled glass support material. A network of broken glass units will be loaded into the reactor vessels. The coating film, size and geometry of glass packing is important in allowing photocatalytically adequate transmittance of light, adequate oxygenation through aeration, and efficient turbulence lateral mixing. Though this particular reactor designs may not be sufficiently theoretically optimised, in reality it is seldom that treatment facilities operate ideally. The study will investigate photocatalytic performance analysis of glass material immobilised titanium dioxide against suspended slurry catalyst in non-perfect-mix batch reactors using multi-chloride substituted phenols.

2. Experimental

2.1. Materials

4-chlorophenol (4-CP) 99% purity, 2,4-dichlorophenol (2,4-DCP) 99%, 2,4,6-trichlorophenol (2,4,6-TCP) 98%, pentachlorophenol (PCP) 97%, and anatase 99.7% titanium dioxide (TiO_2) were purchased from Sigma-Aldrich Logistik GmbH (Schnelldorf, Germany). Phenol and GC grade methanol were purchased from Merk (South Africa). Ultra-pure (UP) water was dispensed by the Millipore Direct Q3 with pump instrument. Reference standard were purchased from PerkinElmer (South Africa division). Contributions to the congress are welcome from throughout the world.

2.2. Catalyst immobilisation

Recycled transparent glass (Schott Duran) of 2 000 g mass was broken to pieces, rinsed with tap water and dried in heating oven at 100 °C for 2 hours. 2 000 mg of anatase titanium dioxide powder was mixed in 1 L of ultra-pure water, magnetically stirred at 200 rpm for 2 hours. The glass was then completely submerged in the catalyst mixture, separated using a sieve and transferred to a high-temperature heating plate. The plate was placed in a furnace (Thermo-power furnace) oven at 500 °C for 48 hours, cooled to room temperature and water submerged for 30 minutes then dried in an incubator oven at 60 °C for 2 hours, and separated to size of minimum unit centre diameter of 8 mm and maximum diameter of 20 mm. A finely thin resistant layer of titanium dioxide (Fig. 1) coating was established. Random glass pieces transparency tests using spectroscopy (WPA Lightwave II, Labotech) recorded average transmittance % of 53 ± 4.4 ($n = 10$). The goal was to establish a thick enough spatial coated catalyst film to facilitate adsorption while allowing adequate incidence light to pass-through at areas perpendicular to the glass surface. The glass packing process into the reactor vessel was neither specific nor pattern-structured, glass units were delicately filled into the vessel.



Fig. 1: Titanium dioxide coated broken glass units

2.3. Photocatalytic reactors installation and setup

In the reactor packing process larger pieces were preferred to maximise the spacing between glass units and minimise light hindrance. The setup was installed in a temperature regulated walk-in reactor room that is

wall-connected to a cold-room of 4 °C set temperature, the wall connection has port-openings that allow transfer of cooled air. The reactor room has a driven air-vacuum that constantly drives the cooling system. The reactor system was configured on a wall-bench structure. Two 400 mL transparent glass reactors vessels were mounted on stands side-by-side (30 cm apart). Each vessel had oxygen (O₂) of 99 % purity delivery tube connected to a regulator, and connected to a longitudinal fizzle nozzle. On either side of the reactor vessels were 3 quartz glass sleeves mounted equidistant from each vessel. Encased in the quartz sleeves were long-arc 400 Watts (Philips HOK 4/120 SE) medium pressure lamps. The reactor on the right shows catalyst-immobilised glass packing represented by positive filling, the size need not be extrapolated from the schematic. The photolysis experimental runs of the network packed reactor used non-catalyst coated glass units of similar size and geometry.

2.4. Analysis

Polychlorinated phenolics and derivative products were analysed using a gas chromatography (GC) system comprising of a clarus 600 GC, clarus 600T mass spectrometer (MS), attached to a turbomatrix 40 trap headspace sampler (PerkinElmer, South Africa division). The chemical separation component was the Elite 5MS GC system capillary column (30 m, 250 µm) from PerkinElmer. Helium (He) carrier gas of 99.999% purity and applied at a flow rate of 1 mL/min. MS interface comprised of an Electron Ioniser (EI) and a high performance mass analyser..

2.5. Data process and modelling

Sigmaplot 11 scientific data analysis graphics computation software was used for data processing and statistical analysis. Aquasim 2.0 computer program for the identification and simulation of aquatic systems was used to simulate and model the photocatalytic oxidation profiles, and parameter estimations.

3. Results and Discussion

3.1. Reactor configuration analysis

The reactor installation under study is not an ideal complete-mix batch system. Complete-mix reactors are assumed to achieve instantaneous mixing that is uniform throughout the reactor, without a designated mixing mechanism the current system mixing is facilitated by rigorous gas bubbling. The oxygen fizzle tube had outlet pores longitudinally pierced below maximum solution height, this is assumed to deliver significant lateral dispersion. The deviation of this setup from traditional batch systems is the glass packing component, the large porous nature of the packing can be viewed as an unstructured randomised network. Performance analysis is a result of each chlorophenols transformation with regards to its independent degradation and conversion, coupled with the generation and accumulation of less substituted derived chemicals under scrutiny. The overall rate of degradation or formation process within each reactor is quantified based on the prevailing resultant process as is it empirically impossible gather data of simultaneous complex photocatalytic processes of multiple related compounds.

3.2. Photocatalytic degradation performance kinetics

The information in the legend-box of the figures corresponds to the different chlorophenols, each compound is colour-coded to aid identification, and the line patterns distinguish the immobilised catalyst set from the photolysis set. One of the objectives of this study was to validate photocatalytic application against photolysis in the configured reactor setup. It is evident from Fig. 2 that photolysis performed poorly in comparison to the catalyst-immobilised set of data. With the exception of phenol, there is a distinct difference in performance over the 6.5 hour period, where near-complete oxidation and degradation of the chlorophenols was achieved. Phenol can be viewed as the stem substituted with chloride ions, the oxidation clipping of all the chloride ions results in phenol. As the most conformationally stable compound, phenol is expected to experience the most oxidation inefficiency that is a result of negative degradation due to accumulation by the structural dehalogenation of the substituted compounds. Fig. 2 is in agreement with this expectation, after a total illumination period there is little change between the initial and final concentrations. The phenol profile does suggest that there is descent degradation in the early periods of the experiments before an increase in recorded in the latter periods, the increase can be attributed to accumulation from the

near-complete transformation of 4-CP amongst other monochlorinated phenolic derivatives not under scrutiny in the study, when the degradation sequence of all chlorophenols is considered. The chlorophenol degradation sequence in Fig. 2 shows that higher chloride-substituted phenol compounds disappear at a faster rate than lower-substituted compounds with the exception of 4-chlorophenol at higher concentrations of the photocatalytic process, while no distinct pattern is observed from the photolysis set. Less than fifty percent of degradation of the compounds was achieved in the photolysis experiments after irradiation of 6.5 hours.

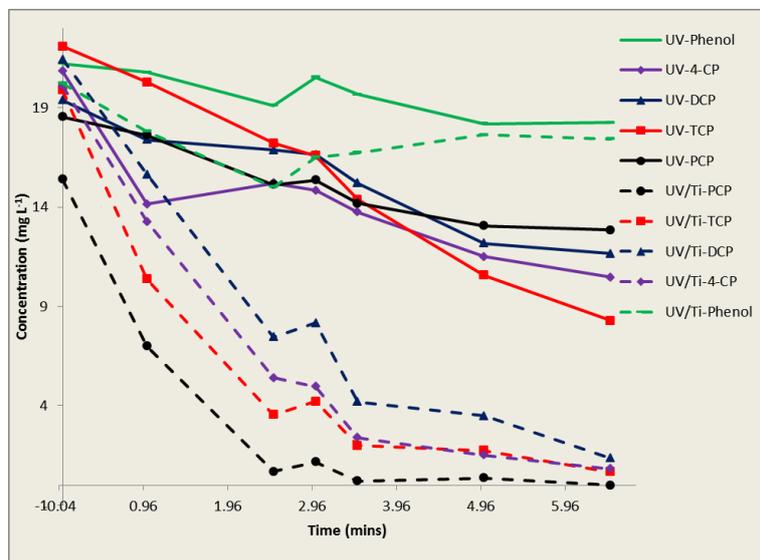


Fig. 2: Photocatalytic degradation profiles of chlorophenols in immobilised catalyst and control sets

The difference in the efficiency of photocatalysis and photolysis can only be attributed to the presence of the catalyst. Though the support material of interest may not be ideal with regards to the criteria identified in some studies, sufficient oxidation can clearly be achieved and justification for this low cost support material suffices. The experimental kinetic adsorption isotherms of chlorophenols and phenol from aqueous solutions onto titanium dioxide were analysed in a different component of the project and are shown in Fig. 3. With the exception of phenol, the four tested chlorophenols were adsorbed on to the catalyst in concentrations directly proportional to their degree of chlorination. Excluding phenol, the order of adsorption onto titanium dioxide is 4-CP < DCP < TCP < PCP. The plots of the inverse of the adsorbed chemical concentration per weight (Q_e) versus the inverse of the final equilibrium solution concentration (C_e) were used to evaluate the Langmuir adsorption constants variables. Four chlorophenols were simultaneously oxidised in open batch systems in this study. Results show that higher level substituted chlorophenols undergo oxidation resulting in the decrease in its concentration and an assumed subsequent formation of a lower level substituted compound in combination with other unrelated derivative species. There are also intermediate chlorophenol compounds which do not form part of the compounds of interest in this study, such as 2-chlorophenol, 2,3-dichlorophenol and 2,3,4,6-tetrachlorophenol that may influence the degradation and conversion processes. The photocatalytic sequence at high concentrations is PCP < TCP < 4-CP \leq DCP. Another measure of control was to attest the immobilised catalyst data versus a suspended catalyst system. This is not a direct comparison as this would kinetically be implausible, it is however a measure of the performance against an ideal perspective and conformational analysis of chlorophenol compounds behaviour. Fig. 4 shows the suspended slurry catalyst treatment of chlorophenols, the degradation sequence reported in the immobilised data set is maintained, and the behavioural profile of phenol is not dissimilar. The major difference is the commentary behaviour of DCP and 4-CP at low concentration, in the immobilised data set DCP was less efficiently removed, this distinction is less apparent in the suspended set. This could be a result of adsorption selectivity of titanium dioxide and the availability of active sites in the suspended catalyst in comparison to the limited available and exposed surface area of immobilised catalyst, and the transformation of oxidised DCP and subsequent formation of 4-CP.

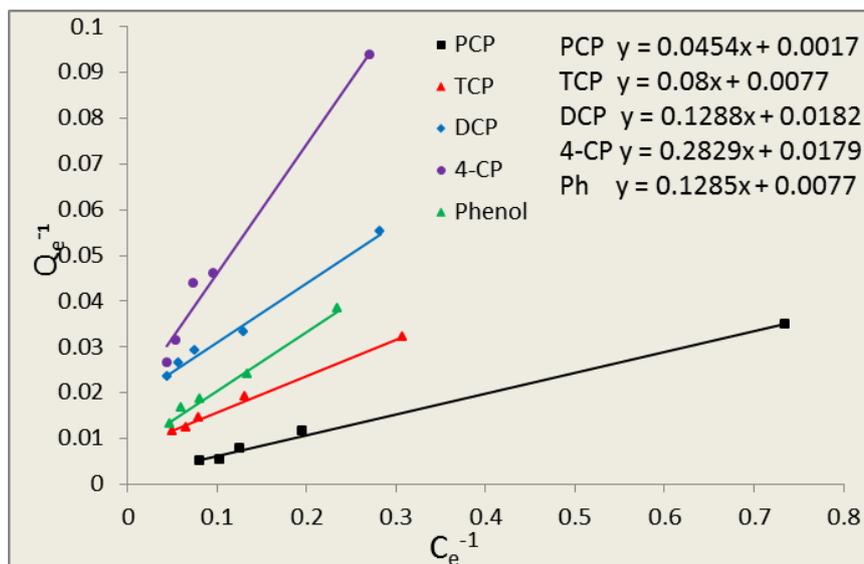


Fig. 3: Langmuir isotherm plots

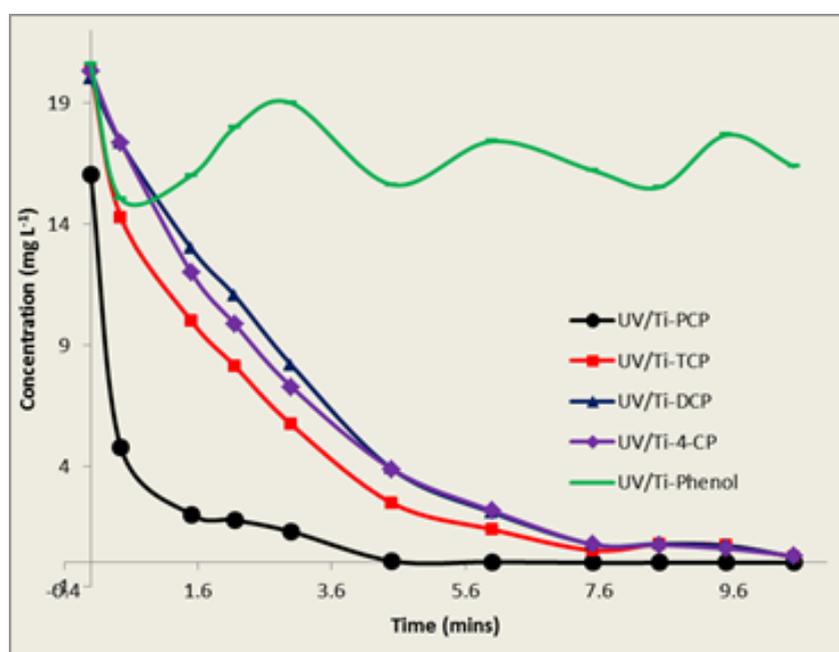


Fig. 4: Photocatalytic degradation profiles of chlorophenols in suspended catalyst

4. Conclusion

This study evaluated the efficiency of recycled glass immobilised titanium dioxide photocatalytic degradation of multi-substituted chlorophenols in batch reactors systems, and compared data to photolysis. The aims were to investigate and determine preliminary application successes of immobilised catalyst on large support materials. The results showed effective oxidation of chlorophenols from high initial concentration by immobilised catalyst. The immobilised catalyst data set was viewed in light of suspended applications and provided insights into preliminary photocatalytic installation effectiveness using simple and low cost support material.

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6. References

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