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The Effect of Reaction Conditions on the Degradation of Phenol by UV/TiO_2 Photocatalysis

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Photocatalysis is a process in which the rate of photoreaction is accelerated in presence of a catalyst. It has gained much interest due to its ability to completely mineralise a variety of organic compounds into carbon dioxide and water. This paper describes the basics of heterogeneous photocatalysis, mainly on TiO_2 and the application of the photocatalytic process to water purification, mainly to remove phenol as well as special emphasis on the effects of; solution pH, dissolved oxygen, catalyst load, initial phenol concentration and UV radiation on the photoactivity. Photocatalytic degradation of phenol was conducted in 1 L solutions of phenol (20 mg/L) in ultrapure water in a batch system. Catalyst concentration was constant at 8 mg/L Titanium dioxide (TiO_2). Concentration of phenol was monitored on a Waters High Performance Liquid Chromatograph (HPLC) and Gas Chromatogram- Mass Spectrometer (GC-MS). Results showed that photo degradation is an effective method for the removal of phenol from wastewaters. The efficiency of the process depends strongly on the experimental conditions.

1. Introduction

The discharge of large amounts of synthetic chemicals such as solvents, plasticisers, insecticides, herbicides and fungicides into the environment through industrial, agricultural, medical and domestic activities has produced significant ecotoxicological problems with serious consequences for all living organisms (Kanakaraju et al., 2014). These substances include phenols which have been classified as priority pollutants by the United States Environmental Protection Agency (USEPA) (Michałowicz and Duda, 2007).

It has been frequently observed that pollutants not amenable to biological treatment may also be characterised by high chemical stability and/or by strong difficulty to be completely mineralized. In these cases, it is necessary to adopt reactive systems much more effective than those adopted in conventional purification processes.

Photocatalysis can be defined as the acceleration of a photoreaction by the presence of a catalyst at a solid surface usually a semiconductor. It uses natural or artificial light to irradiate the catalyst (semiconductor) to promote degradation (Lazar et al., 2012). Photocatalysis, one of the most powerful advanced oxidation systems is based on the generation of hydroxyl radicals. The hydroxyl radical is an extremely powerful oxidation agent, second only to Fluorine in power (Fujhima et al., 2008). Photocatalysis is a versatile, low-cost and environmentally benign treatment technology for a host of pollutants. These may be of biological, organic and inorganic in origin within water and air. The efficient and successful application of photocatalysis demands that the pollutant, the catalyst and source of illumination are in close proximity or contact with each other (Ibhadon and Fitzpatrick, 2013).

In this study, the photocatalytic degradation of phenol in the presence of titanium dioxide (TiO_2) nano-particles and UV light was investigated, with emphasis on the effects of; solution pH, catalyst load, initial phenol concentration and UV radiation intensity was assessed.

2. Methods and materials

2.1 Chemical reagents

Phenol reagent was purchased from Merck (Johannesburg,South Africa). HPLC grade acetonitrile (99.9 % purity) was purchased from Glassworld Anatase titanium dioxide (TiO_2) was purchased from Sigma-Aldrich (Sigma-Aldrich Pty Ltd). All solutions were prepared using ultrapure water produced in a Milli-Q, Millipore Direct Q3 Unit (supplied by Microsep, Johannesburg, South Africa). Hydrocholric acid (32 %) and sodium hydroxide pellets were purchased from Glassworld.

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2.2 Experimental setup

Degradation studies were conducted in a fed-batch reactor with photons for catalyst activation supplied by a medium pressure 400 W UV lamp immersed just above the pollutant solution housed in a double jacket quartz sleeve, which served as the cooling system for the lamp. Temperature control in the reactor was achieved by circulating cold water through the outer cavity of the quartz sleeve. The reactor contents in all batches were aerated at a flow rate of 10 mL/min. Thorough mixing of the contents of the reactor was achieved by continuous agitation with a magnetic stirrer. The experimental reaction time was set at 100 min. Aliquots of 2 mL were withdrawn from the reactor at 10 min intervals using a micro-syringe for further analysis. The reactor system was a closed system as UV light is very harmful (Figure 1).

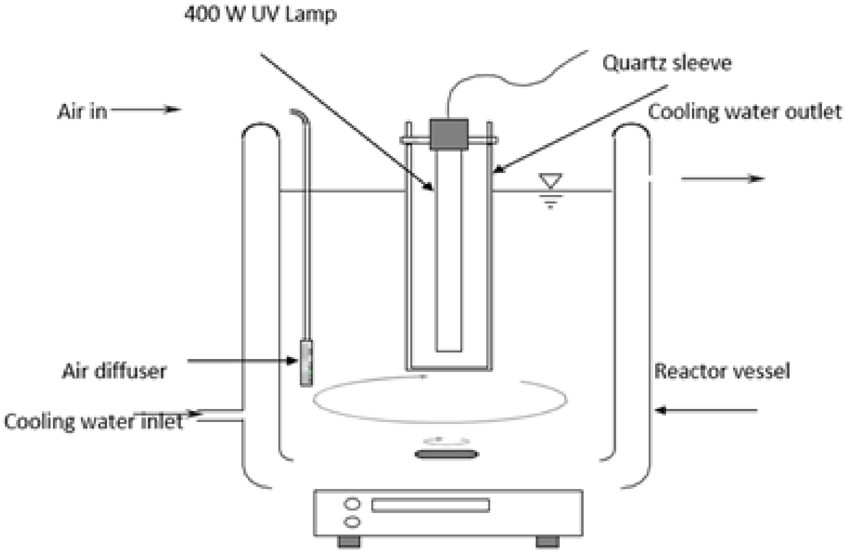

Figure 1: Experimental set-up of photocatalytic fed-batch reactor (adopted from Bamuza-Pemu and Chirwa, 2011).

2.3 Batch studies

Experiments were run in triplicates and average values are reported. Samples were then transferred into 0.5 mL micro-centrifuge tubes where they were then centrifuged for 10 minutes to separate suspended catalyst from the solution before GC-MS analysis.

2.4 Analytical methods in degradation studies

2.4.1 High performance liquid chromatography

Concentrations of the phenol were monitored on a Waters HPLC (Waters 2695 separation module with a photo diode array – Waters 2998 PDA detector. Phenol and the intermediate compounds were separated on Synergi Fusion-RP C18 (150 x 4.6 mm, 4 µm) column (Phenomenex) and Empower software for data analysis. A binary mobile phase consisting of 60 % acetonitrile (A) and 40 % water (B) was used for elution of compounds at a flow rate of 1.2 mL/min at 25 °C, injection volume was 10 µL with B operated in the isocratic mode.

2.4.2 Gas chromatography mass spectrum

The phenol solution samples were analysed using a 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 5 MS GC system capillary column from PerkinElmer. Helium (He) carrier gas of 99.99 % 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. This was used to measure the concentration of phenol during the course of photocatalysis.

3. Results and discussion

3.1 Effect of solution pH on the photoactivity

Evidently, the degradation reaction can proceed in a wide range of pH (Figure 2), the conversion of phenol changed with the pH of the solution and average results were reported. For an initial solution containing phenol 100mg/L, 12.1 % conversion of phenol at pH 3, 5.7 % at pH 5, and 5.6 % at pH 7 were observed within 1 h of irradiation. Overall, the conversion of phenol increased with the increase of pH when the reaction was conducted in alkaline media, and the conversion rate of phenol at the same irradiation time dropped to 3.6 % at pH 9 and increased to 25.2 % at pH 11. The increasing activity at higher pH attributed to the increasing concentration of phenolate ions. The stabilities of the transition states of phenol or phenolate and singlet oxygen determine the rate of photo-oxidation. The electronic interaction takes place between the calculated lowest unoccupied molecular orbital (LUMO) of singlet oxygen, located at −0.98 eV, and calculated HOMO of phenolate, located at −2.69 eV, or of phenol, located at –9.81 eV. An increase in the difference between the energy of the LUMO of singlet oxygen and the energy of the HOMO of the organic substrate results in weaker electronic interaction. Therefore, phenol is less reactive than phenolate in the photo-oxidation process. The reaction time, 60 minutes, was a limiting factor and it did not paint a picture of the full reaction kinetics. Longer reaction time is to be investigated.

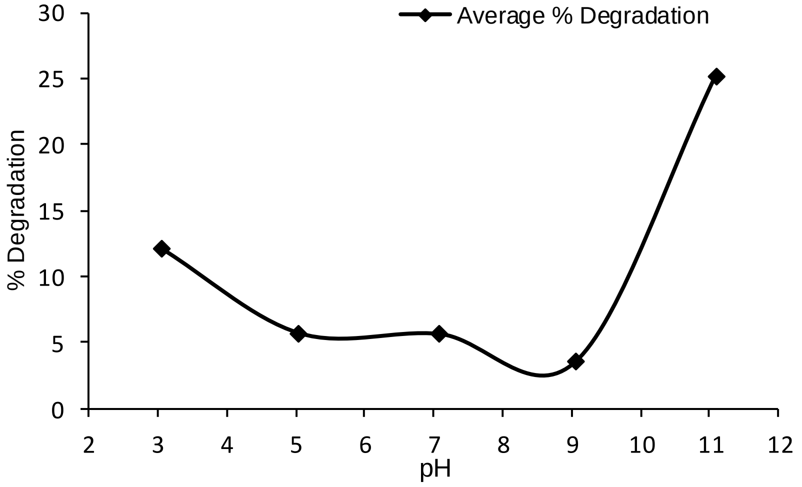

Figure 2: The % phenol degradation with change in pH.

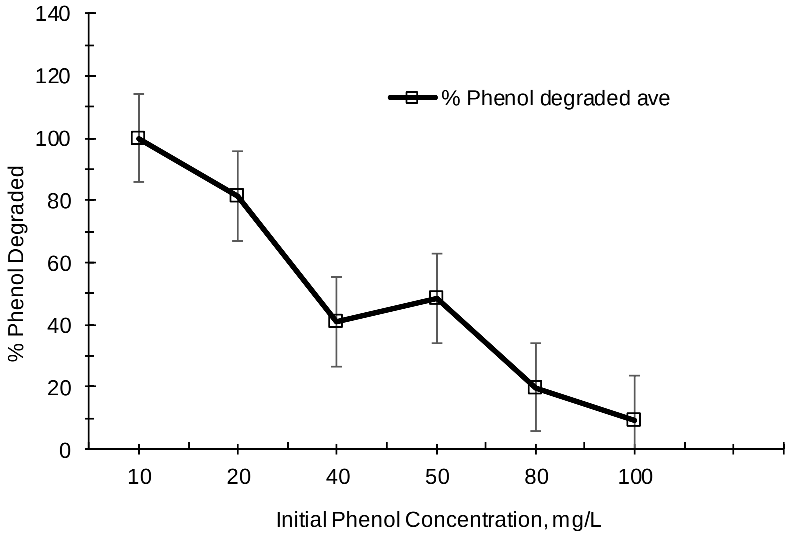

Figure 3: The graph depicts the phenol degradation profile for different initial phenol concentrations at a constant TiO_2 concentration of 20 mg/L.

3.2 Effect of initial phenol concentration

Degradation efficiencies are governed by the availability and effective contact of reactive species in solution and on the catalyst surface with pollutant species. Phenol is relatively soluble in water and its main reaction zone for photocatalytic degradation is believed to be in the bulk liquid. The sharp decrease in phenol concentration beyond initial phenol concentration of 10 mg/L can be attributed to the fact that high concentration of pollutant in water saturates the TiO_2 surface. This leads to a reduction in the photonic efficiency and deactivation of the photocatalyst especially as formation of reactive radical species ($\cdot OH$ and $O_2^{-\cdot}$) remain constant at a particular catalyst concentration (20 mg/L) and light intensity (Fujhima et al., 2000). The degradation profile of phenol at different initial concentrations over a constant catalyst concentration (20 mg/L) can be seen in Figure 3.

3.3 TOC analysis

TOC analysis showed (Table1) there was no significant difference in the NPOC amounts before and after photocatalysis although results from HPLC and GC-MS analysis showed significant amounts of phenol removal. This can be attributed to the simultaneous formation of degradation intermediates during the course of phenol photocatalysis, therefore longer reaction times were required in order to achieve significant differences in NPOC.

Table1: Chemical composition of P-25 Degussa.

Initial Phenol Concentration, mg/L	NPOC degraded, mg/L	%NPOC degraded
10	0.012	1.15
20	0.010	1.11
30	0.007	0.7
50	0.0009	0.089
100	0.0142	1.42

3.4 Effect of catalyst loading on photoactivity

Degradation efficiency was tested on pre-determined TiO_2 concentrations, in the range of 2 mg/L to 10mg/L at a constant phenol concentration of 100 mg/L. The highest degradation was obtained at a TiO_2 concentration of 8mg/L as shown in Figure 4**.** The degradation efficiency gradually increased from 2 % to 14 % at a TiO_2 concentration of between 0mg/L to 5 mg/L. There was a rapid increase in the degradation efficiency from 29 % to 71 % between TiO_2 concentration of 6 mg/L at a TiO_2 loading of 8 mg/L and 10mg/L respectively. This can be attributed to the fact that the amount of TiO_2 is above saturation level, the light photon adsorption co-efficient decreases radially and the excess photocatalyst creates a light screening effect that leads to the reduction in the surface area exposed to irradiation and thus reduces the photocatalytic efficiency of the process.

3.5 Effect of UV light intensity on the photoactivity.

Different control conditions were experimented on and the results are depicted in Figure 5. Each of the control conditions had a significant effect on the photocatalytic activity. The least phenol degradation was observed when the reaction was illuminated with UV radiation of 9W. The amount of phenol degraded reduced from 70.6 % to 11.1 % when using the 400W and 9 W UV lamps respectively. Higher light intensity resulted in higher phenol degradation. The conversion depended strongly on the incident light intensity, thus, increasing the light intensity from 9 W to 400 W enhanced phenol degradation in a remarkable way. The photonic nature of the photocatalysis reaction has outlined the dependency of the overall photocatalytic rate on the light source used (Tshuto et al., 2017). These results are attributed to the fact that there were relative low amounts of photons in the reaction system at low light intensity; on the other hand, at high intensity, photons were present in excessive amounts leading to more reactive species generation and more destruction of phenol; this proved that higher catalyst activity occurred under high light intensity.

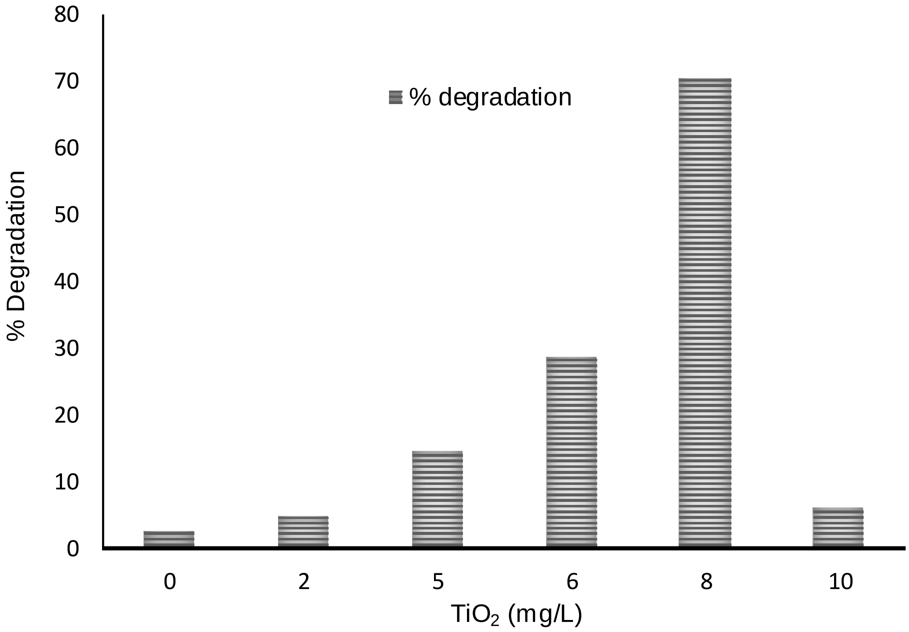

Figure 4: The effect of TiO_2 (mg/L) concentration on the phenol degradation.

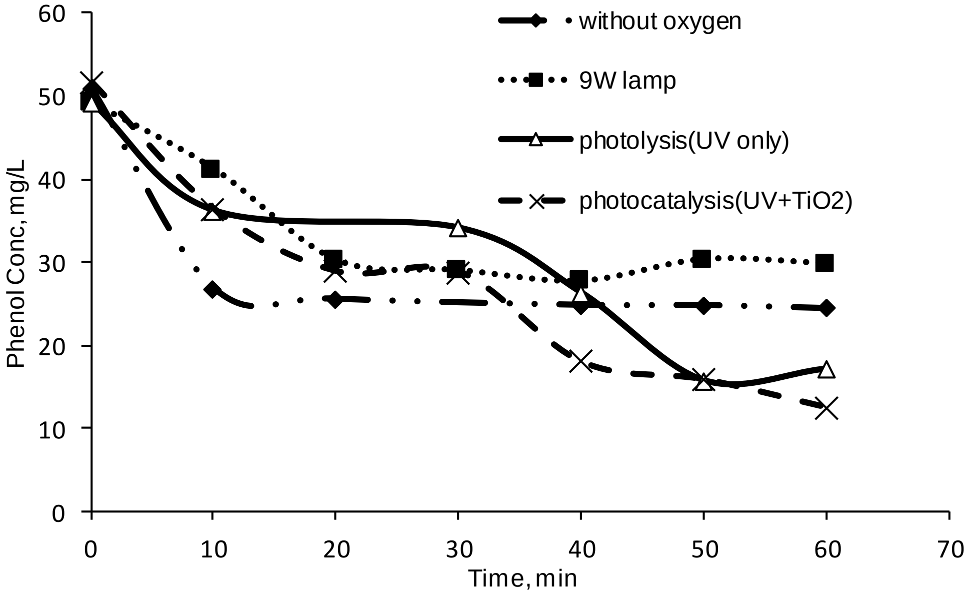

Figure ***Error! No text of specified style in document.****: The graph shows the degradation profile for the different control conditions.*

The removal of aeration also saw a great reduction in phenol removal. Photocatalysis and photolysis did not differ much in terms of overall phenol removal, however, the rate constant varied during the course of reaction. This suggests that the catalyst makes no significant difference in the photodegradation and this was attribute to turbidity of the phenol solution thereby inhibiting the photoreaction by blocking the light from reaching catalyst surface.

5. Conclusions

Results showed that photo degradation is an effective method for the removal of phenol from wastewaters. The efficiency of the process depends strongly on the experimental conditions. The amount of catalyst, UV irradiation time, pH and light intensity were important parameters in the degradation process. The rate constants for the different parameters were evaluated and indicated that titanium dioxide photocatalyst P-25 was very active in phenol degradation. Therefore, combined UV/TiO_2 process may be applied as an effective process for the removal of phenol from aquatic solutions such as industrial wastewaters and polluted water resources. However, photocatalysis and photolysis showed no significant difference in the photodegradation and this was attributed to turbidity. The slurry reactor configuration has shown its limitations and going forward, a fixed bed reactor and synthesis of a suitable catalyst are to be explored.

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