Solar Photodegradation of Phenol using a Composite Catalyst of Silica and TiO_2

Mervyn Khune, John Akach, and Aoyi Ochieng

Abstract— In this study, solar photocatalysis was employed to remove phenol from synthetic wastewater. Composite catalysts of different compositions were synthesized and applied for solar photocatalysis. The effect of the silica loading, composite loading, initial phenol concentration and initial solution pH on the photodegradation of phenol was investigated. It was found that a decrease in silica loading and initial concentration of phenol led to an increase in photodegradation. Increasing the composite loading and pH, on the other hand, led to an increase in photodegradation up to a limit. The best photodegradation was achieved at a catalyst composition of 60% TiO_2, composite loading of 5 g/L, phenol concentration of 15 ppm and solution pH of 4. At these conditions, there was a 100% degradation of phenol within 5 hours.

Keywords—Advanced oxidation processes, silica, solar photocatalysis, titanium dioxide, phenol.

I. Introduction

THE treatment of industrial wastewaters such as phenol has been a problem for some time. Therefore, there has been a need to develop and employ treatment technologies capable of dealing with the hazardous pollutants present in many industrial waste streams [1]. Phenols are discharged from wastewater from industries such as coking, synthetic rubber, plastics, paper, oil refineries, petrochemical, ceramic, steel, conversion processes and phenolic resin industries [2-3]. Phenolic compounds found in wastewater present a serious environmental problem due to their poor biodegradability, high toxicity and ecological effects [4]. Ingestion of liquid products containing concentrated phenol by humans can cause serious gastrointestinal damage and even death [5]. Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations [6].

Therefore, various methods such as biological treatment, activated carbon adsorption, solvent extraction, chemical oxidation and electrochemical methods have been developed for the treatment of phenol wastewater [7-12]. Most of these methods suffer from high cost, low efficiency, and generation of toxic by-products [13].

One of the most cost effective, robust and attractive treatment methods of removing phenols in wastewater is solar photocatalysis. Photocatalysis can completely degrade organic pollutants into harmless inorganic substances such as CO_2 and H_2O under normal sunny conditions using semiconductors. Upon the discovery of photocatalytic properties of TiO_2 (semiconductor) and its effectiveness to generate hydroxyl radicals in the presence of UV light more research was undertaken in this respect [8]. TiO_2 has a low band gap (3.2eV), low cost, non-toxic nature, strong oxidising power and high resistance to chemical or photo-induced corrosion [14].

Most photocatalysis studies have utilised nanophase TiO_2 which has been challenging to separate from wastewater. Therefore, TiO_2 has been supported onto various materials to improve its separation from wastewater [15]. One of the most promising immobilization methods has been through the use of binders such as silica gel. Photocatalysis has mostly been carried out using UV light. However, UV light is costly and this has motivated the use of sunlight as the energy source for TiO_2 [16].

In this work, treatment of phenolic wastewater was investigated using solar photocatalytic degradation employing TiO_2 supported on silica. The main focus of the work was to investigate the effects of catalyst composition, catalyst loading, phenol initial concentration and solution pH on the photodegradation of phenol.

II. Methodology

A. Equipment Setup

The reactors used for photocatalysis were 250 mL borosilicate glass conical flasks. The flasks were put in an open-top orbital shaker to mix the phenol and catalyst during the experiment. The photodegradation experiments took place under solar irradiation during sunny days at a roof at the Vaal University of Technology.

B. Materials

TiO_2 (technical grade) and colloidal silica (Ludox HS-30) were purchased from Sigma-Aldrich. Phenol was obtained from Labchem. HCl was purchased from Ace Chemicals and NaOH was bought from Merck.

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C. Experimental procedures

1) Catalyst preparation

The composite catalysts were prepared by binding TiO_2 using silica xerogel. In this method appropriate amounts of TiO_2 and colloidal silica were magnetically stirred in a bottle for an hour. The slurry mixture was then spread on glass plates and dried at 60^oC to remove the water. The dry samples were then screened to a size range of between 38 and 75 µm. The screened powders were then washed with 0.1 M HCl to remove the excess alkalinity. The excess acidity of the catalyst was then removed by washing the catalysts several times with distilled water. After drying at 60^oC, the final composite catalyst product was obtained.

2) Phenol photocatalysis degradation

Wastewater was synthesized by dissolving phenol in distilled water to prepare the desired concentration of phenol. A volume of 200 mL of the phenol solution was poured into 250 mL glass conical flasks. The pH of the solutions were then adjusted using HCl or NaOH, the pH values being measured using a pH meter (Thermo Scientific, OrionStar A111). Then, appropriate amounts of catalyst of the desired composition were added into the conical flasks. The flasks were then placed in the open-top orbital shaker which was put on the roof. Samples of the phenol solution were taken hourly and filtered using 0.45 µm GHP syringe filters (Pall Acrodisc). The concentration of phenol was then analysed using a UV-Vis spectrophotometer (PG Instruments, T60) at a λ_{max} of 270 nm. After the experiment, turbidity of the solution was measured in the UV-Vis spectrophotometer at a wavelength of 800 nm. To maintain consistent and reliable results, each parameter was investigated on the same day under the same atmospheric conditions and samples analysed on the same day of the experiment.

III. Results and Discussion

A. Effect of catalyst composition

The effect of catalyst composition was investigated by using 4 different catalyst composites with different TiO_2 loadings. The results (Figure 1) show an increase in the photodegradation of phenol with an increase in the TiO_2 content of the composite catalyst. This is due to the fact that TiO_2 is the photoactive component in the composite and increasing the TiO_2 leads to an increase in photodegradation [17]. From the results, it can be seen that there was some instability in the first 2 hours of photodegradation. This can be attributed to the brown colouration of the solution during the first two hours when phenol was degraded to coloured intermediates [18]. The coloured intermediates interfered with UV-vis measurements thus resulting in inaccurate readings.

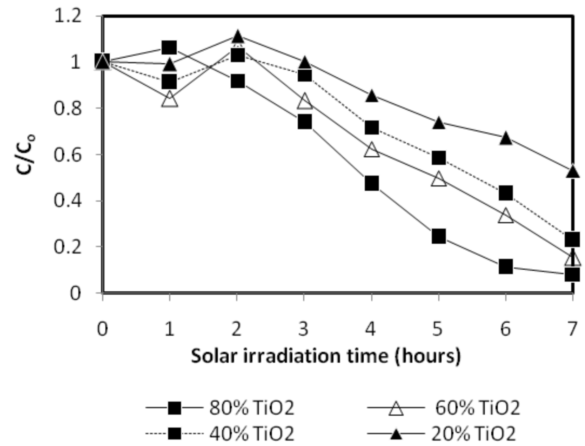

Fig. 1 Effect of catalyst composition on the photodegradation of phenol. (C_0 = 20 ppm, composite loading = 3 g/L)

Turbidity measurements were carried out after the reaction to investigate the separation of the TiO_2 from silica during photocatalysis. The results (Table 1) show a stable turbidity reading with an increase in the TiO_2 content from 20 to 60%. However, increasing the TiO_2 content to 80% resulted in a spike in solution turbidity. This is due to the fact that increasing the TiO_2 content beyond 60% of the composite catalyst lead to a decrease in the silica content of the composite resulting in a weaker binding of the TiO_2.

Table 1
Effect of catalyst composition on solution turbidity

	Turbidity			
Catalyst Composition	*80% TiO_2*	*60% TiO_2*	*40% TiO_2*	*20% TiO_2*
Concentration	0.046	0.004	0.007	0.001

An increase in the TiO_2 content in the composite beyond 60% was thus found to increase photodegradation but reduce the attachment efficiency of the silica. Therefore, the best catalyst composition was chosen after considering both degradation and attachment efficiency. The catalyst with a composition of 60% TiO_2 was thus chosen as the best.

B. Effect of composite loading

The effect of composite loading was investigated using the best catalyst composition. The results (Figure 2) show an increase in the photodegradation with an increase in composite loading. However, there was no significant increase in photodegradation beyond 5 g/L.

It was reported by Malato and co-workers [19] that the rate of photo demineralization generally increases with catalyst loading towards a limiting value at high TiO_2 concentrations. The limiting factor has been attributed to attenuation of light penetration into the reactor at high catalyst loadings. Therefore, 5 g/L composite loading was chosen as the best.

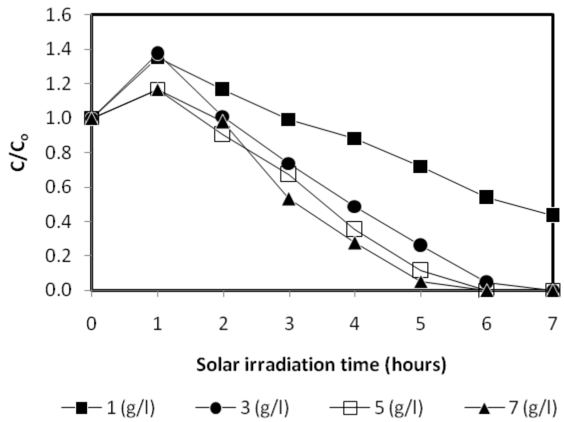

Fig. 2 Effect of composite loading on phenol photodegradation. (Catalyst composition = 60% TiO_2, C_0 = 20 ppm)

C. Effect of substrate initial concentration

The best catalyst loading of 5 g/L was used to investigate the effect of initial concentration on the photodegradation of phenol. The results (Figure 3) show an increase in the removal of phenol with a decrease in the initial concentration of phenol. For example, complete degradation for 10 ppm was reached in 3 hours while for 25 ppm took 7 hours. Ochieng and co-workers, [16] reported that the path length of photons entering the solution increases with decreasing substrate initial concentration, thereby increasing the number of photons absorbed by the catalyst.

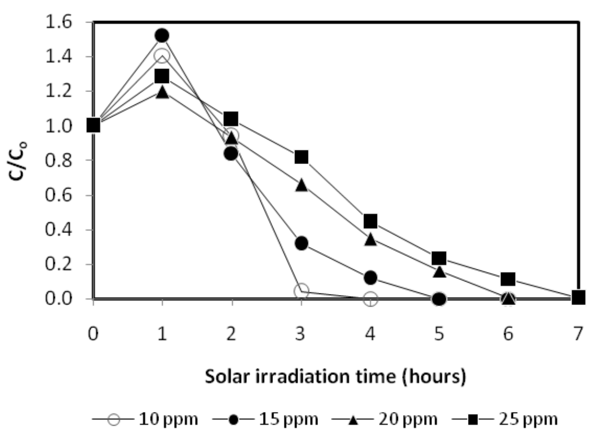

Fig. 3 Effect of initial concentration on the photodegradation of phenol. (Composite loading = 5 g/L; catalyst composition =60% TiO_2)

D. Effect of solution initial pH

Solution pH determines the surface charge properties of the photocatalyst, consequently the behaviour of the pollutant and availability of hydroxyl radicals. This makes it an important parameter in photocatalysis to be investigated. The results of the pH experiment (Figure 4) show a decrease in the photodegradation of phenol with an increase in the solution pH. For example, only a degradation of 47% was achieved at a pH of 10 while at pH 4 the degradation increased to 96% within 4 hours.

In their study, Shahrezaei and co-workers [20] reported that the photodegradation of the phenol was more efficient under acidic conditions, than under basic conditions. The authors explained that when solution $pH<pH_{zpc}$, the electron-hole formation and adsorption of phenol on the TiO_2 are favoured. In their experiment, Apollo and co-workers [21] reported that the photodegradation of phenol was low in basic conditions. Their explanation was that phenol exists as negatively charged phenolate ion at higher pH medium. The catalyst composition has a negatively charged surface at the solution $pH > pH_{zpc}$. Hence, coulombic repulsion between the phenolate anions and the negatively charged catalyst surface decreases the adsorption onto the surface of the catalyst.

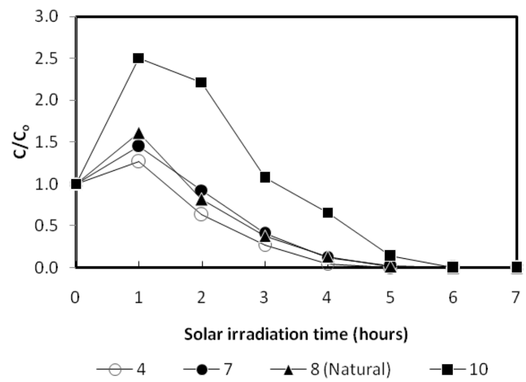

Fig. 4 Effect of pH on phenol photodegradation. (C_0= 15 ppm, composite loading = 5 g/L, catalyst composition = 60% TiO_2)

In their experiment, Shahrezaei and co-workers [20] found an optimum solution pH for phenol to be 3. Similar results have been obtained in this study.

IV. Conclusion

Solar photocatalytic degradation of phenol using TiO_2-silica was investigated focusing on the effect of catalyst composition, composite loading, substrate initial concentration and solution pH. The best photodegradation was obtained when using a catalyst composition of 60% TiO_2, composite loading of 5 g/L, phenol concentration of 15 ppm and solution pH of 4. At these conditions, 100% degradation was obtained in 5 hours. These results indicate that solar photodegradation of phenol using a composite of TiO_2 and silica is an effective technique for the treatment of petroleum wastewater.

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