



Journal of Applied Sciences

ISSN 1812-5654

science
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Application of a Semiconductor Oxide-Based Catalyst in Heterogeneous Wastewater Treatment: A Green Technology Approach

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Abstract: The use of chlorine bleaching in study and pulp industry has resulted in chlorinated phenol contaminated wastewater from that industry. A new wastewater treatment process, sonophotodegradation of 2,4,6-trichlorophenol (TCP) in a heterogeneous aqueous system was investigated and reported in this study. TCP was degraded with ultrasonic or ultraviolet irradiation or a combination of both, in the presence of titanium dioxide semiconductor catalyst (anatase and/or rutile), in order to study the effectiveness of sonocatalysis, photocatalysis and sonophotocatalysis oxidation in a batch sonophotoreactor system. Preliminary studies presented in this study suggested that rutile worked well under sonocatalysis, anatase was the preference for photocatalysis and sonophotocatalysis benefited from a combined rutile and anatase mixture catalyst. Sonophotocatalysis oxidation of TCP demonstrated a degradation that was higher than sonocatalysis or photocatalysis individually while the first-order kinetics rate constants indicated that sonophotocatalysis degradation of TCP was synergistic with a positive value of 0.0203 in the presence of the mixture catalyst.

Key words: Sonocatalysis, photocatalysis, sonophotocatalysis, sonophotodegradation, chlorophenol, anatase, rutile

INTRODUCTION

Chlorinated phenolic compounds are widely used synthetic organic compounds, which are used as either synthesis intermediates in pesticides or as bleaching agent. These organic compounds are also commonly found in industrial waste water and are frequently detected in polluted water (Czaplicka, 2004; Gao *et al.*, 2008). Chlorinated phenolic compounds or chlorophenols such as 2,4,6-trichlorophenol (TCP) is a derivative of the chlorinated phenolic family. The TCP molecule contains a chlorine atom each at the carbon position of the 2nd, 4th and 6th on the phenolic ring. These compounds are polar compounds and as such, their polarity decreases with an increase in Cl substitution on the benzene ring. The solubility of the TCP compound has been reported to be 0.434 g/L at 25°C (Czaplicka, 2004) but dissolves very slowly in distilled water, typically taking two days (with continuous stirring) to dissolve 100 mg L⁻¹. TCP has been used directly or indirectly in paint, pharmaceutical, pesticide, solvent, wood, paper and pulp industries since the 1930s and is very commonly detected in those industrial wastewater or effluent. This chemical is also

used as a fungicide, herbicide, insecticide, antiseptic, defoliant and as a glue preservative. Waste disposal and water treatment methods such as incineration of municipal waste and disinfection of water with chlorine, also generates TCP. Most uses of TCP have been discontinued due to its toxicity, mutagenic and xenobiotic properties, but several fungicides still require the use of TCP for synthesis purposes (USEPA, 2000; Chaliha and Bhattacharyya, 2008; Radhika and Palanivelu, 2006). TCP, a weak acid, is classified as a probable human carcinogen by the by the United States Environmental Protection Agency (University of Berkeley, 2007; Gao and Wang, 2007; USEPA, 2000; Chaliha and Bhattacharyya, 2008; Radhika and Palanivelu, 2006). TCP has xenobiotic characteristics, which makes it resistant to biodegradation. Therefore, it has to be decomposed before being discharged into rivers and lakes to prevent biomagnified toxicity to aquatic life, especially, its accumulation via the food chain. The toxicity and recalcitrant of TCP in the environment is because of its C-Cl bond, which is very stable and also the relative location of the chlorine atoms to the hydroxyl group in the TCP molecule (Tzou *et al.*, 2008). The conventional

technologies used in the treatment of chlorophenols consist of three categories: physical treatment, such as reverse osmosis, activated carbon adsorption (Joseph *et al.*, 2009a), biosorption (Sharain-Liew *et al.*, 2011), solvent extraction and hyperfiltration; chemical treatments, such as chemical degradation, chemical oxidization, incineration, wet oxidation, hypercritical oxidation, high-pressure impulsive discharge and low temperature plasma; biological treatment, such as activated sludge, membrane separation technique and aerobic/anaerobic methods. Adsorption, which is a common physical treatment process, is nothing more than a phase transfer technique. The pollutant is transferred from the liquid state to the solid state (instead of being mineralized or destroyed) and further treatment is required prior to disposal. This physical method is useful for fast removal of the pollutant from a specific location but requires further treatment elsewhere. In chemical treatments, high costs are normally required and in addition, reaction by-products and other chemicals are released into the environment as a result of the treatment process. The toxicity of TCP has rendered biological treatments to be ineffective in decomposing TCP and other chlorophenols. This has resulted in biodegradation treatment to be ineffective (Wang *et al.*, 2000; Krishnaiah, 2003; Jung *et al.*, 2001; Aksu and Yener, 2001). As these systems and technologies do not destroy or degrade the pollutant molecules but merely transfer the liquid pollutant into a solid one, which has to be treated before burying in landfills while the use of chemicals in wastewater treatment causes secondary reactions, which may require further treatment, there is a need to develop a cheap, innovative and regenerative method which uses Green Technology to completely degrade water based organic pollutants to harmless molecules *in situ*. Advanced oxidation process has been successfully employed to treat wastewater contaminated with chlorophenols in recent years (Joseph *et al.*, 2009a; Li Puma *et al.*, 2008). Previously, using a combined batch-annular sonophotolysis reactor, the feasibility of using ultrasonic sound waves and ultraviolet irradiation to degrade the TCP molecules (Joseph *et al.*, 2011) in a non-catalytically reaction were successfully demonstrated. In that paper, the intensities of the ultrasonic sound waves and ultraviolet irradiation were investigated and documented. In this paper, using only a batch type reactor, we present the heterogeneous sonophotocatalysis degradation reaction in batch mode using two types of crystalline structured titania.

SEMICONDUCTOR -BASED CATALYST

The chemical and physical composition of TiO₂ or titania is a very well known and well researched material

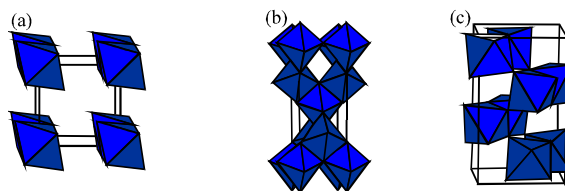


Fig. 1(a-c): Crystalline structure of, (a) Rutile, (b) Anatase and (c) Brookite

due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties. It exists in four mineral forms that are, anatase, rutile, brookite and Titanium dioxide (B) or TiO₂(B). Anatase type TiO₂ has a crystalline structure (Fig. 1) that corresponds to the tetragonal system (with dipyrimal habit) and is used mainly as a photocatalyst under UV irradiation. Rutile type TiO₂ also has a tetragonal crystal structure (with prismatic habit) (Fig. 1). This type of titania is mainly used as white pigment in paint. Brookite type TiO₂ has an orthorhombic crystalline structure (Fig. 1). TiO₂(B) is a monoclinic mineral and is a relatively newcomer to the titania family. TiO₂ is, therefore, a versatile material that is used in various applications such as paint pigments, sunscreen lotions, electrochemical electrodes, capacitors, solar cells and even as a food coloring agent (Meacock *et al.*, 1997) including toothpastes. The preparation of TiO₂ films has even demonstrated futuristic application use such as thin dielectrics in Dynamic Random Access Memory (DRAM) storage capacitors (Campbell *et al.*, 1999). In the last decade, however, TiO₂ has been developed and used as a photocatalyst for indoor and outdoor air purification and for the purification and remediation of contaminated waters loaded with low concentrations of toxic organic pollutants (Ollis and Al-Elkabi, 1993).

MATERIALS AND METHODS

Materials: 2,4,6-Trichlorophenol (98%) obtained from Aldrich was used without further purification. Anatase (powder, 99.8% trace metals basis) and rutile (powder, 99.995% trace metals basis) were obtained from Aldrich.

Procedure: A commercial 1 L jacketed glass vessel (Fig. 2a) was used as a batch-type sonophotoreactor with a diameter of 10 cm and the depth of 20 cm. The sonophotoreactor was thermostated by a water jacket and kept at a constant 30°C for all experiments by means of a temperature controller (Thermo Haake K10). A modified syringe (Fig. 2b) was used for sample extraction from point X (Fig 2a). An ultrasonic horn, 20 kHz, 750 W direct-

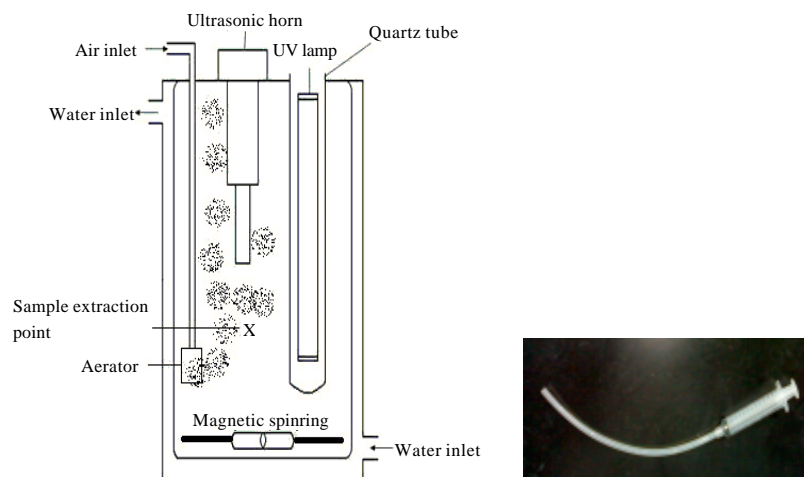


Fig. 2(a-b): Schematic diagram of the batch-type (a) sonophotoreactor (b) Modified syringe used for sample extraction

immersion horn sonicator (Sonics and Materials 750 W Vibra Cell™) was used to generate ultrasonic sound waves in the sonophotoreactor. The tip of the horn has a radiating surface area of 4.91 cm², which is sufficient to radiate solutions with a volume capacity of 500 to 1000 mL. A 4 W UV BLB (Sylvania) lamp, was used to provide a source of UV-A radiation with a maximum peak of 365 nm. This lamp was placed inside a quartz lamp sheath and submerged into the solution as shown in Fig. 2a. Prior to the experiment, the lamp was switched on for 20 min (before placing into the quartz lamp sheath). This was done in order to bring the low-pressured mercury lamp up to working temperature. The effective radiating length of the UV tube was 7.8 cm (with the radiating surface area equal to 37.96 cm²) after the lamp ends were masked with Teflon tape, due to instability of UV intensity in these regions. A radiometer (Solar Light, model PMA2100) with a UVA detector (Solar Light, model PMA2110) was used to measure the UV-A intensity from the lamp encased in the quartz lamp sheath. The UV lamp and US horn are located at the sides (1 cm from the vessel's walls) and together they were placed in a triangle with the aerator. The residual concentration of TCP was determined by using a UV-Vis spectrophotometer (Varian Cary 50 conc) at the detection wavelength of 295 nm (Shih *et al.*, 1990; Michizoe *et al.*, 2004). In this study, the sonicator was set at 50% amplitude in a continuous wave mode which gave an acoustic intensity of 10 W cm⁻² and the UV-A lamp intensity was set at 6 mW cm⁻² for all experiments. All experiments were dark experiments and repeated in triplicates with the average value taken and plotted into graphs. Four milliliter of sample was extracted for each sampling (every 15 min). The total amount of sample taken for each experiment was 4% of the total solution volume (500 mL).

RESULTS AND DISCUSSION

Three grams of catalyst (anatase or rutile) and 3 grams of anatase-rutile catalyst with the ratio of 1:1, was used to study the sonocatalysis, photocatalysis and sonophotocatalysis degradation of 500 mL, 50 ppm TCP. Fig. 3 shows the residual concentration TCP after 1 h of degradation for (a) Sonocatalysis, (b) Photocatalysis and (c) Sonophotocatalysis. It is clearly shown that rutile worked well under sonocatalysis, anatase was the preference for photocatalysis and sonophotocatalysis benefited from a combined rutile and anatase mixture catalyst in a ratio of 1:1. After 60 min contact time, sonocatalysis reduced the 50 ppm TCP to 24.8 ppm (anatase), 19.42 ppm (rutile) and 22.4 ppm (anatase/rutile). Under the same contact time parameter, photocatalysis reduced the 50 ppm TCP to 10.3 ppm (anatase), 39.6 ppm (rutile) and 28.3 ppm (anatase/rutile). While combining sono and photodegradation reduced the 50 ppm TCP to 15.1 ppm (anatase), 30.1 ppm (rutile) and 1.2 ppm (anatase/rutile). This clearly demonstrates the effectiveness of combining both types of semiconductor catalyst under sonophotodegradation. Anatase-type catalyst has a higher band-gap value of 3.2 eV as compared to rutile-type catalyst but rutile-type catalyst can absorb radiation that is nearer to visible light. However, photocatalysis favors the use of anatase-type catalyst over rutile-type catalyst due to its conduction band position which allows for better reducing power as compared to rutile-type catalyst (Li Puma *et al.*, 2008). Sonophotocatalysis oxidation of TCP demonstrated a degradation that was higher than sonocatalysis or photocatalysis individually and after 1 h of degradation,

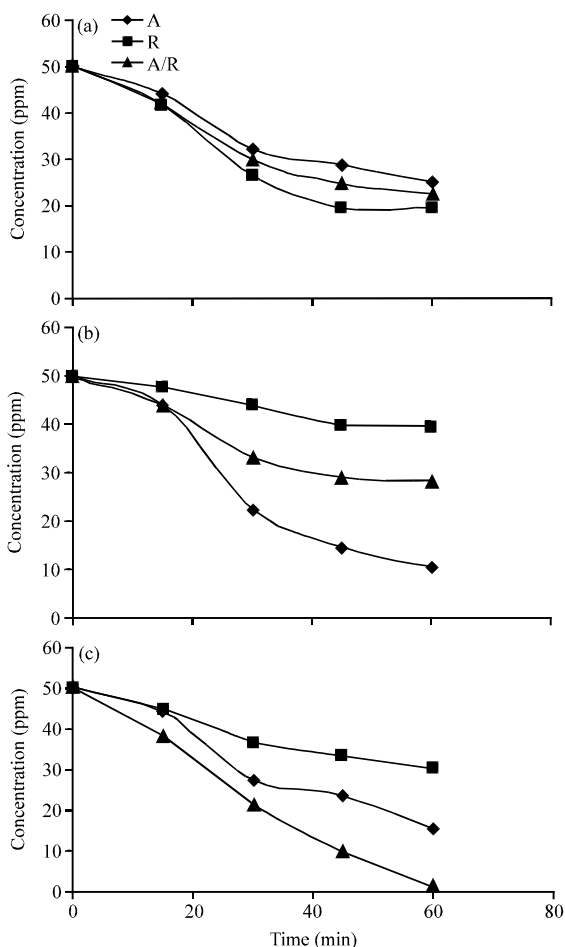
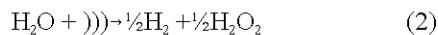


Fig. 3(a-c): Residual concentration of TCP after 1 hour of degradation for, (a) Sonocatalysis, (b) Photocatalysis and (c) Sonophotocatalysis

almost all of the TCP was degraded. In sonocatalysis, the semiconductor oxide was activated by the ultrasonic sound waves to generate OH radicals. It is these radicals that contributed to the breakdown of the TCP. The exact mechanism is still under investigation. Ultrasonic sound waves can also generate OH radicals by means of sonolysis process (Joseph *et al.*, 2011).

The degradation of TCP during sonolysis is due to the oxidation of the TCP molecule by hydroxyl radicals generated during the sonication (sonolysis or sonodecomposition of water) by means of cavitation according to Eq. 1 and 2:



where,))) denotes sonication.

Table 1: The general mechanism of the photocatalytic reaction process on irradiated TiO₂

Process	Reaction steps	Eq. No.
Electron-hole pair formation	TiO ₂ + hν → TiO ₂ + OH (or TiO ₂ ^{•+})	3
(semiconductor valence band hole and conduction band electron)	TiO ₂ + O ₂ → TiO ₂ + HO ₂	4
Electron removal from the conduction band	TiO ₂ + H ₂ O ₂ + H ⁺ → TiO ₂ + H ₂ O + OH	5
Hole trapping	TiO ₂ + 2H ⁺ → TiO ₂ + H ₂	6
	H ⁺ + H ₂ O → OH + H ⁺	7
	H ⁺ + HO → OH	8
Oxidation of organic pollutant molecules	OH + O ₂ + C _x O _y H _(2x+2y+2) → xCO ₂ + (x-y+1)H ₂ O	9
Nonproductive radical reactions	TiO ₂ + OH + H ⁺ ? TiO ₂ + H ₂ O (recombination)	10
	2OH → H ₂ O ₂	11
	2HO ₂ → H ₂ O ₂ + O ₂	12
	2OH + H ₂ O ₂ → H ₂ O + O ₂	13
	2OH + HCO ₃ ⁻ → CO ₃ ²⁻ + H ₂ O	14

Cavitation is also positively influenced by the presence of particulate in the solution and by the temperature of the solution (Joseph *et al.*, 2011).

In the photocatalysis process, the general mechanism of the photocatalytic reaction process on irradiated TiO₂ is shown in Table 1. The process of photodegradation of pollutants by TiO₂ starts by the absorption of UV radiation equal or higher than the band gap value of 3.2 eV for anatase or 3.0 eV for rutile onto the TiO₂ particles creating a photogeneration of holes and electron pairs (Eq. 3, Table 1) in the semiconductor valence band (hole) and conduction band (electron). It must be noted that although both anatase and rutile type TiO₂ absorb UV radiation, rutile type TiO₂ can also absorb radiation that are nearer to visible light. However, anatase type TiO₂ exhibits higher photocatalytic activity than rutile type TiO₂ due to its conduction band position which demonstrates stronger reducing power as compared to rutile type TiO₂. These energized holes and electron can either recombine (Eq. 10, Table 1) and dissipate the absorbed energy as heat or be available for use in the redox reactions (Eq. 4-6, Table 1). As such, photocatalysis favors anatase instead of rutile.

In sonophotocatalysis, the combined use of ultrasonic sound waves and ultraviolet A irradiation in the presence of anatase and rutile catalysts contributed to a significant degradation rate as compared to the use of ultrasonic sound waves and ultraviolet A irradiation individually. Due to the preference of anatase by ultraviolet A irradiation and rutile by ultrasonic sound waves, a catalyst mixture of anatase and rutile in the ratio of 1:1 was most effective in the degradation of TCP and contributed to the synergistic effect of this process. The synergy effect of the sonophotocatalysis process can be represented as shown in Fig. 4.

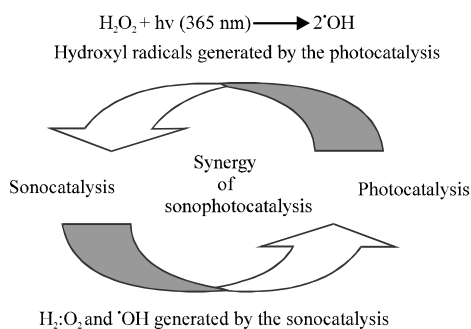


Fig. 4: Schematic diagram of the sonophotocatalysis synergistic effect

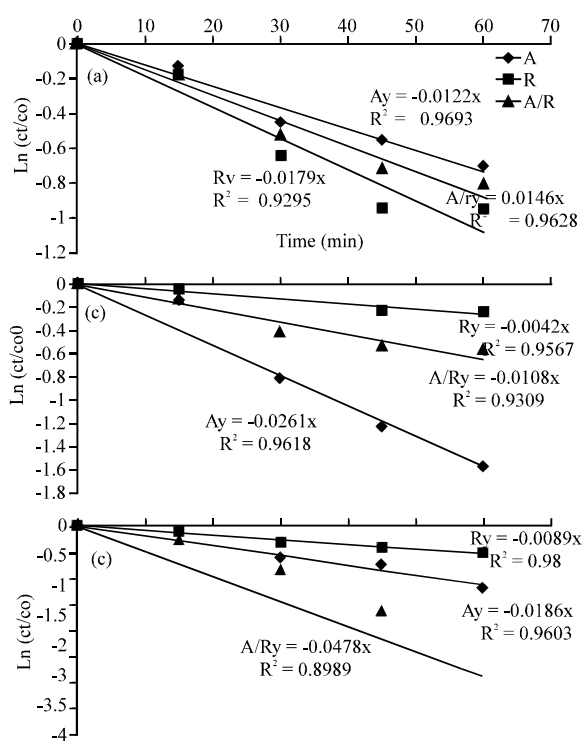


Fig. 5(a-c): Kinetic constant plots for the sonocatalysis, (a) photocatalysis, (b) and sonophotocatalysis (c) at constant solution temperature of 30°C

Reaction kinetics study was conducted in this research work. It was determined that the sonocatalysis, photocatalysis and sonophotocatalysis degradation reaction schemes complied with the first order reaction as the linear regression coefficient (R^2) was more than 0.9. Figure 5 shows the first order reaction kinetic analysis. Under sonocatalysis degradation scheme, rutile-type catalyst gave the highest reaction rate of 0.0179 min⁻¹, followed by anatase/rutile catalyst which

was 0.0146 min⁻¹ and finally anatase-type catalyst, which gave 0.0122 min⁻¹. While under photocatalysis degradation scheme, anatase-type catalyst gave the highest reaction rate of 0.0261 min⁻¹, followed by anatase/rutile catalyst which was 0.0108 min⁻¹ and finally rutile-type catalyst, which gave 0.0042 min⁻¹. Combining the sono and photodegradation scheme, anatase/rutile-type catalyst gave the highest reaction rate of 0.0478 min⁻¹, followed by anatase-type catalyst which was 0.0186 min⁻¹ and finally rutile-type catalyst, which gave 0.0089 min⁻¹. The synergism between the photocatalysis, sonocatalysis and sonophotocatalysis was determined using of first-order rate constants, according to Eq. 2a, which was modified from our previous paper (Joseph *et al.*, 2009a, b):

$$\text{Synergy (s)} = \frac{k_{\text{sonophotocatalysis}} - k_{\text{sonocatalysis}} + k_{\text{photocatalysis}}}{k_{\text{sonophotocatalysis}}} \quad (2a)$$

In this equation, if “S” is greater than 0, the effect is synergistic, if “S” is equal to 0, the effect is additive and if “S” is less than 0, the effect is antagonistic. From Fig. 5c and by means of calculation using equation 1, it is clearly shown that the synergism of sonophotocatalysis in this degradation scheme is at (+) 0.0203.

CONCLUSION

The use of sound and light energy (ultrasound and ultraviolet irradiation), which has Green Technology characteristics, to degrade 2,4,6-trichlorophenol in the presence of titania catalyst has proven to be effective in degrading TCP. Preliminary studies of the reaction kinetics in the sonophotodegradation of 2,4,6-trichlorophenol in a heterogeneous aqueous system, suggest that rutile worked well under sonocatalysis, anatase was the preference for photocatalysis and sonophotocatalysis benefited from a combined rutile and anatase mixture catalyst. Combining both types of catalyst and degradation schemes resulted in a synergistic effect, which accelerated the degradation of TCP. This paper has demonstrated the effectiveness of treating chlorinated phenol contaminated wastewater using sonophotodegradation and suitable semiconductor catalyst. This work has also provided water treatment specialist and pollution experts an effective, low-cost and innovative water treatment method with Green Technology applications. This research work has promising commercializing prospect. With the development of suitable treatment plants, this application is expected to treat high volume of wastewater in situ, in shorter treatment time and at a lower cost than current methods.

ACKNOWLEDGMENTS

This research was supported by the Center of Research and Innovation, University Malaysia Sabah (Grant No. FRG0203-SG-1/2010) and is gratefully acknowledged.

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