

# Photocatalytic Degradation of Salicylic Acid and Reduction of Cr(VI) using TiO<sub>2</sub>

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**Abstract**— Water pollution caused by organic and inorganic contaminants represents an important ecological and health hazard. In this study the photocatalytic reduction of Cr(VI) and degradation of salicylic acid (SA) in aqueous suspensions using commercial TiO<sub>2</sub> was investigated. The effect of operating parameters such as photocatalyst loading, initial pollutant concentration and pH were optimized in aqueous solution containing salicylic acid alone and hexavalent chromium alone. The performance of the photocatalyst reactor was evaluated on the basis of salicylic acid removal and metal ion reduction. The rate of salicylic degradation for the ternary salicylic acid /Cr(VI)/TiO<sub>2</sub> system were generally lower than that for the respective binary salicylic acid/TiO<sub>2</sub> systems. This could be attributed to partial catalyst deactivation to some extent.

**Keywords**— Chromium, photocatalysis, photocatalyst, salicylic acid.

## I. INTRODUCTION

THE rapid development of civilization and industrial activities has led to a series of environmental problems. For many years, large amount of pollutants have been discharged into the environment intentionally or accidentally, including toxic metals in water with a great health concern [1]. Various organic and inorganic wastewaters have been produced and discharged from metal plating, mining, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries [2]-[3]. Among the different industrial wastewaters, tannery effluents co-contaminated with organic and inorganic compound generated in the dyestuffs, textile, and leather cause serious effects to human health and aquatic life. Treatment of such pollutants from contaminated water is a complex challenge throughout the world, as the two components need to be treated independently using an effective and robust technique [4]. Different from the organic components such as salicylic acid, toxic metallic ions generally are not degradable and have an infinite lifetime, thus they may accumulate in living tissues, causing various serious diseases and environmental problems [5]. Some of the metal ions are actually necessary for human body in trace amounts while others are carcinogenic or toxic, damaging the nervous system, kidney, liver, skin, bones, or teeth [3]. The removal of toxic metals in an effective and economic way has been a critical issue for the environment improvement [6]. Among the heavy

metal ions, Cr(VI) is one of the toxic, carcinogenic and mobile contaminant originating from various industrial processes such as pigment production, and leather tanning. In aquatic environments, chromium exists mostly in the hexavalent chromium Cr(VI) and trivalent chromium Cr(III) states. Anionic Cr(VI) is far more mobile and toxic than Cr(III) and more difficult to remove from water [7]-[8]. Similar to many other metal cations, however, aqueous Cr(III) can be readily precipitated as Cr(OH)<sub>3</sub> or removed by adsorption and ion exchange. Thus, reduction of chromium from its hexavalent to trivalent states simplifies its removal from effluent and also reduces its toxicity and mobility [9-10].

Photocatalytic technology has been studied since 1970s and widely explored for the degradation of organic and inorganic contaminants in the presence of certain semiconductors as catalyst under light exposure [3]-[11]. This technology is based on the photo-induced highly reactive electron/hole (e<sup>-</sup>-h<sup>+</sup>) pairs on TiO<sub>2</sub> under illumination by light of energy greater than its bandgap. Holes and various oxygen containing radical species (OH, O<sub>2</sub><sup>-</sup>, HO<sub>2</sub><sup>•</sup>) play an important role in the photocatalytic oxidation of organic pollutants, while photo-generated electrons are critical to the photocatalytic reduction of heavy metal ions [12]. Whenever various catalysts (oxides, sulphides, etc.) have been tested under comparable conditions for degradation of the same compound, TiO<sub>2</sub> has proved to have the highest photocatalytic activity with a large resistance to photo-corrosion. Titania has universally been recognized as one of the better photocatalysts in heterogeneous photocatalysis applications as it combines two important complementary features for a photocatalyst: good UV absorption efficiency for the light harvesting process and good absorption capacities, due particularly to the density of OH<sup>-</sup> groups of amphoteric character [13]. Schrank et al. [14] investigated the UVA/TiO<sub>2</sub> treatment of model solutions containing the dye luranzol S kong alone, Cr(VI) alone, as well as their mixture as a function of the substrate concentration and solution pH and reported that the rates of both dye oxidative degradation and Cr(VI) reduction in their mixture were faster than the respective rates in the single substrate systems.

The aim of this study was to investigate simultaneous photocatalytic degradation of salicylic acid and reduction of chromium (VI) using titanium oxide. The effect of operating parameters such as initial pH, initial concentration and TiO<sub>2</sub> catalyst dosage in the presence of UV irradiation for

treatment of synthetic wastewater were investigated.

## II. EXPERIMENTAL

### A. Material

TiO<sub>2</sub> Degussa P25 was purchased from Merck Chemicals (Pty) Ltd., R.S.A. Salicylic acid (Aldrich +99%) was prepared by dissolving the solid in distilled water. All chemicals were of analytical reagent grade and used without further purification. Cr(VI) solution was prepared by dissolving an appropriate amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in distilled water. For simultaneous degradation runs, solution was prepared by mixing the corresponding volume of each starting solution of single substrates.

### B. Photocatalysis Experiments

The photocatalytic experiments were carried out at room temperature ( $\pm 25$  °C) using a shaker. Experimental set up consists a UV lamp that was placed inside the reactor box *ca* 4 cm above the batch reactors inside the shaker. Aqueous solution volume of 100 ml containing either the salicylic alone, metal alone or their mixture was used throughout. An 18W UV lamp with a maximum emission of 253.7 nm was used. The solution was left to equilibrate for 30 min in the dark before the lamp was switched on. In most cases, experiments were performed at an initial pH of 6.5. In those cases where runs were carried out at basic or acidic conditions, the initial pH was adjusted adding the appropriate amount of 1 M NaOH or H<sub>2</sub>SO<sub>4</sub> as needed. Samples of about 5 mL periodically draw were centrifuged at a rotational speed of 14000 rpm to remove TiO<sub>2</sub> and then analyzed with respect to salicylic acid conversion, and Cr(VI) reduction.

### C. Analytical methods

The quantitative estimation of the salicylic acid was carried out using a UV-Visible spectrophotometer, model-118 at  $\lambda_{\max}$  of 300 nm. The Cr(VI) ion concentration was analysed by Atomic absorption spectroscopy (AAS).

## III. RESULTS AND DISCUSSION

### A. Effect of pH solution on single substrate: Cr(VI) or salicylic acid

The reduction of Cr(VI) at different initial pH over time under different pH values is shown in Fig. 1. The Cr(VI) reduction gradually declined, with an increase in pH values. Higher reduction efficiency was obtained when experiments were performed in acidic solutions than that in alkaline solutions. At pH 2, the reduction rate was 75.3%, however, at pH 8, the reduction rate was approximately 49%. This can be explained by the negatively charged CrO<sub>4</sub><sup>2-</sup> that can associate with hydroxyl groups on composite photocatalyst surface via electrostatic attraction with positively charged Ti-OH leading to a substantial reduction [15]. The decreased photoreduction of Cr(VI) at increased pH values is due to the electrostatic repulsion between negatively charged CrO<sub>4</sub><sup>2-</sup> and the

negatively charged surface of the photocatalyst.

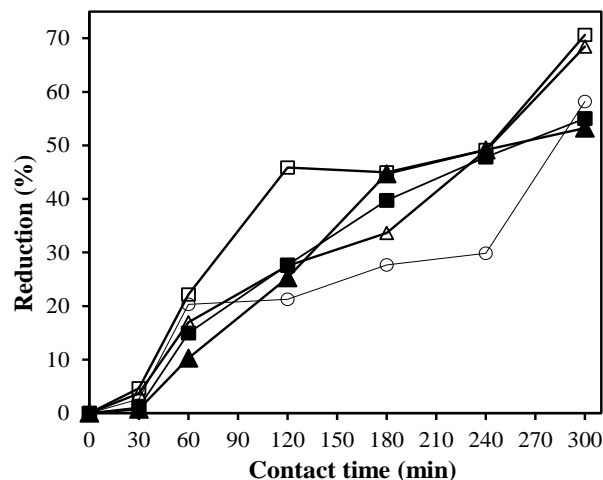


Fig.1. Effect of initial pH solution on photocatalytic reduction of Cr(VI): pH 2 (□); pH 3 (Δ); pH 4 (○); pH 5 (■); pH 8 (▲)

The effect of initial pH solution on the photodegradation of salicylic acid is shown in Fig. 2 where the behavior exhibited in Fig. 1 is also observed. Photodegradation was higher at acidic conditions than in basic conditions. At pH 2 degradation was about 85% and at pH 8 it was 60%. As seen from Fig. 2, degradation was strongly dependent on the solution pH and was substantially hindered at alkaline conditions. At pH 2 salicylic degradation was about 85 % and at pH 8 it was 60%. The effect of pH is more complicated. The isoelectric point for TiO<sub>2</sub> was reported to be 6.5 [16]. The surface charge of TiO<sub>2</sub> becomes negative or positive depending if the pH is above or below the isoelectric point. Thus, in strong acidic and basic conditions TiO<sub>2</sub> exists in the forms of TiOH<sub>2</sub><sup>+</sup> and TiO<sup>-</sup>, respectively. SA is a weak acid and acts in a similar manner existing as a positive or negative ion in strongly acidic or basic conditions. In consequence, the same polarity of charge on the surface and the SA molecule results in an electrostatic repulsion between them which possibly reduces the contacts of active radicals and model substance and thus lowers the degradation rate. In addition, decrease of OH radical production at strongly basic condition has been assumed which might also contribute to the degradation rate at pH 8 [17]. The effect of pH has been contradictory in earlier studies. Hidaka et al. [16] found that the adsorption of SA on sol-gel coated TiO<sub>2</sub> surface was the strongest in acidic pH, whereas the photocatalytic degradation was fastest in alkaline solutions (pH 9) where adsorption was the weakest.

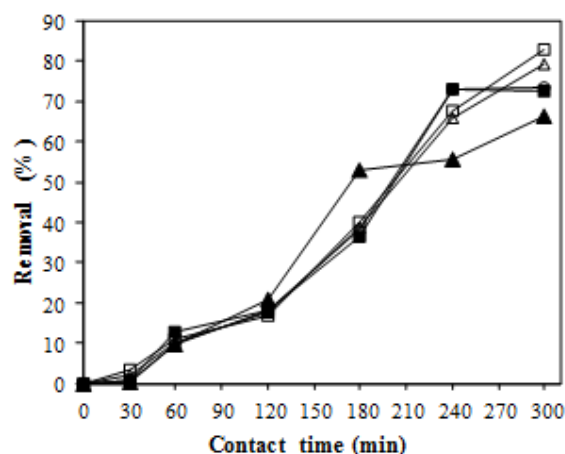


Fig. 2 Effect of initial pH solution on photocatalytic degradation of salicylic acid: pH 2 (□); pH 4 (Δ); pH 7 (○); pH 8 (■); pH 10 (▲)

**B. Effect of catalyst concentration on single substrate: Cr(VI) or salicylic acid**

Figure 3 shows the photoreduction trends of Cr(VI) at different TiO<sub>2</sub> concentration. It was observed that the photoreduction increased when the catalyst concentration was increased from 0.1 to 0.5 g/L. At 0.5 g/L the increased is not substantial showing that the catalyst has reached its maximum performance. Decreased photoreduction efficiency at higher catalyst dosage has been observed in photocatalytic reactions [18]. This behavior may be attributed to the shielding at higher concentrations where the TiO<sub>2</sub> photocatalyst reduces the penetration of light to the solution.

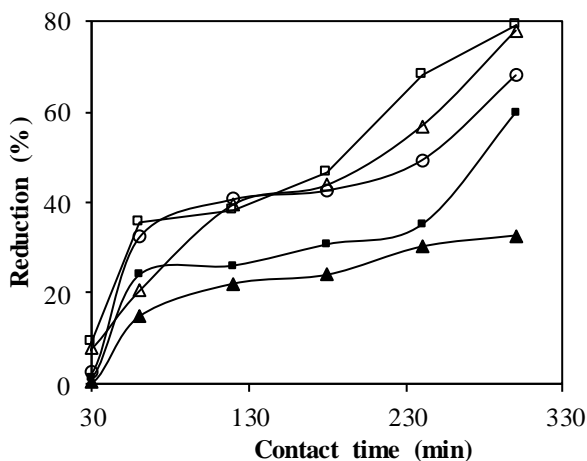


Fig. 3 Effect of initial TiO<sub>2</sub> concentration on photocatalytic reduction of Cr(VI): 0.1 g/L (□); 0.2 g/L (Δ); 0.3 g/L (○); 0.4 g/L (■); 0.5 g/L (▲)

In general, any catalyst will suffer from deactivation to an extent during its service. It is observed in Fig. 4 that initially the degradation of salicylic reduced with an increase in photocatalyst concentration. This was more pronounced at 0.5 g/L photocatalyst concentration which can be due to the partial deactivation of activated molecules by collision with ground state molecules. When the photocatalyst concentration exceeded 0.4 g/L, the degradation efficiency decreased thus causing light scattering and a screening effect while reducing the photocatalytic activity of the composite photocatalyst. The

results suggested that an optimal concentration of the photocatalyst is necessary for efficient degradation.

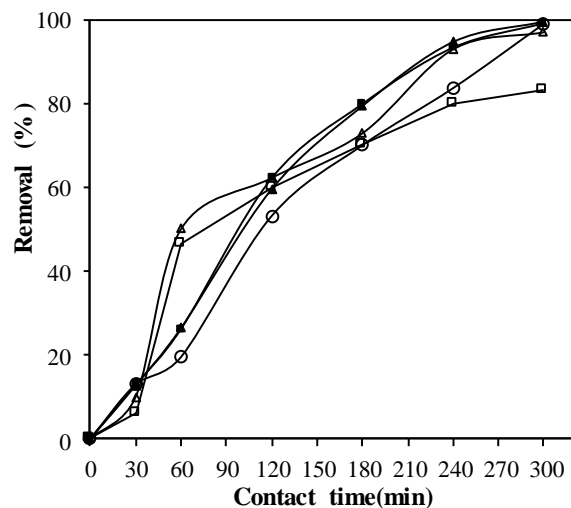


Fig. 4 Effect of initial concentration TiO<sub>2</sub> on the photocatalytic degradation salicylic acid: 0.1 g/L (□); 0.2 g/L (Δ); 0.3 g/L (○); 0.4 g/L (■); 0.5 g/L (▲)

**C. Effect of initial solution concentration on single substrate: Cr(VI) or salicylic acid**

The effect of initial Cr(VI) concentration on Cr(VI) photoreduction was investigated over the range of 2 to 10 mg/L (Fig. 5). Cr(VI) reduction efficiency gradually decreases with an increase in initial concentration of Cr(VI). After 200 min, the reduction of Cr(VI) was 76.7% at initial metal concentration of 2 mg/L and 32.5% at concentration of 10 mg/L under the same operating conditions. The slow photocatalytic reduction of Cr(VI) in the absence of organic compounds is not due to the deactivation of the photocatalyst, however, due the net photocatalytic reaction in a completely inorganic aqueous solution is the three electron reduction of Cr(VI) to Cr(III) with oxidation of water to oxygen, which is a kinetically slow four-electron process [19].

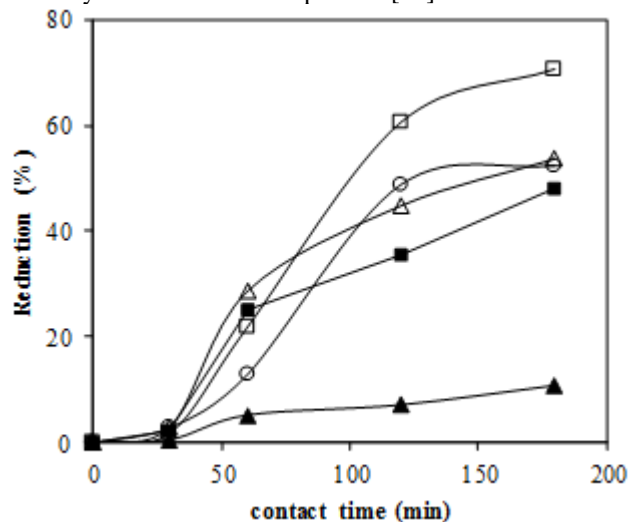


Fig. 5 Effect of initial concentration on the photocatalytic reduction of Cr(VI): 2 mg/L (□); 4 mg/L (Δ); 6 mg/L (○); 8 mg/L (■); 10 mg/L (▲)

In Fig. 6, it can be seen that as the initial concentration increased, the degradation decreased. This result can be described by considering the competition for absorption of the limited quantity of available photons by the salicylic acid. The salicylic acid degradation as function of concentration was faster with an initial concentration of 50 mg/L compared to 10 mg/L. These results might be described by the fact that at higher concentrations more SA molecules are in the vicinity of the catalytic surface and ready to react with constantly emerging short-lived hydroxyl radicals. These results are consistent with the study conducted by Vilhunen et al. [20] where the salicylic acid degradation as function of concentration was determined with catalyst sample TiO<sub>2</sub> T300 and it was found faster with an initial concentration of 75 mg/L compared to 10 mg/L.

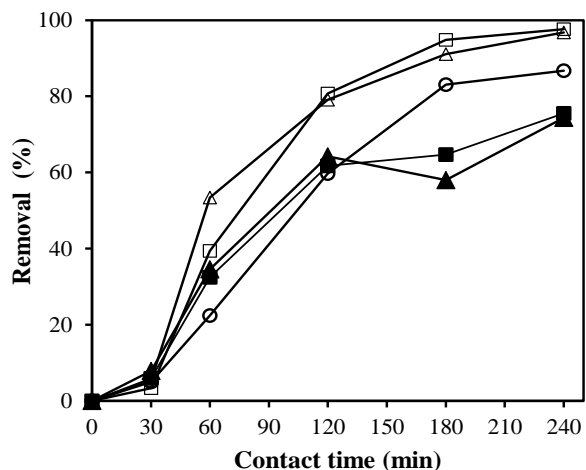


Fig. 6 Effect of initial concentration on the photocatalytic degradation of salicylic acid 10 mg/L (▲); 20 mg/L (■); 30 mg/L (○); 40 mg/L (Δ); 50 mg/L (□);

#### D. Photocatalytic reaction with multiple substrate: Cr(VI) and salicylic acid

The wastewater contaminated by toxic heavy metals often co-exists with organic pollutants in actual wastewater pollution systems. Theoretically, the photocatalytic reduction of Cr(VI) on TiO<sub>2</sub> should be more efficient in the metal-organic-TiO<sub>2</sub> system than in the single system due to the accelerating effect by the preferential photocatalytic oxidation of the organics. In such metal-organic-TiO<sub>2</sub> system, the organic compound receives holes from valence band directly or indirectly, and is oxidized [21]. Thus increasing the photoreduction efficiency of Cr(VI) by suppressing the electron-hole recombination. In an attempt to understand how salicylic acid influences Cr(VI) reduction under photocatalytic conditions, Cr(VI) reduction was analyzed on the systems containing different initial Cr(VI) acid concentration. A higher reduction of Cr(IV) was observed in a binary system than is a single system (Fig. 6 and 7).

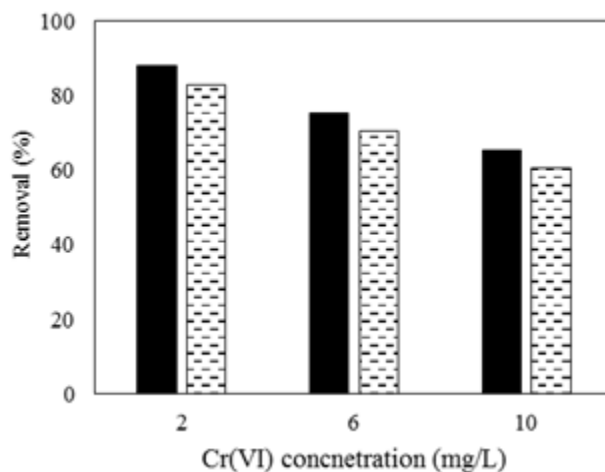


Fig. 7 Effect of Cr(VI) initial concentration on salicylic degradation (black bars) over TiO<sub>2</sub> and final Cr(VI) reduction (hatched bars). Condition: C<sub>0</sub>= 50 mg/L; pH= 2

#### IV. CONCLUSION

The aim of this study was to investigate the heterogeneous photocatalytic degradation of salicylic acid and reduction of Cr(VI). It was observed that variation of the TiO<sub>2</sub> photocatalyst concentration plays an important role in degrading pollutants. The present study indicated that the photocatalytic degradation efficiency initially increases with photocatalyst concentration and then decreased at high values due to light scattering and screening effects. The most interesting result of the study was that the highest degradation of SA with TiO<sub>2</sub> was achieved at higher initial concentration. The presence of salicylic acid significantly improved the photoreduction of Cr(VI) ion into non-toxic Cr(III) ion.

#### ACKNOWLEDGMENT

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