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PHOTOOXIDATION OF ISOPROPANOL AND ACETONE USING TiO_2 SUSPENSION AND UV LIGHT

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INTRODUCTION

Photoexcitation of the bulk titanium dioxide (TiO_2) particle promotes valence band electrons (e^-) into the conduction band leaving positive holes (h^+). The hole reacts with surface hydroxyl groups or molecular water to form adsorbed hydroxyl radicals ($OH^\bullet$) which may dissociate into the bulk solution as a free $OH^\bullet$. Photooxidation reactions of persistent and hazardous organic contaminants present in aqueous waste streams may take place on the TiO_2 surface or in the bulk solution[1-3]. Typically these organic contaminants contain aromatic and/or halogenated functional groups. Their oxidative destruction to CO_2 or smaller polar organic molecules that are readily biodegradable, such as alcohols and ketones, is usually considered an effective treatment.

However, in considering the use of TiO_2 photocatalytic degradation to treat water intended for human consumption, the reaction products and photodegradation kinetics of small polar organic compounds must be carefully considered. Such compounds are highly soluble and do not adsorb strongly to the TiO_2 surface and so they may therefore be fairly resistant to photodegradation. In this study, photocatalytic degradation of some polar organic compounds such as isopropanol and acetone has been investigated. The eventual objective is to provide a suitable photocatalyst for the final processing step in NASA's Water Recovery System (WRS). Isopropanol and acetone were selected as test compounds since they were detected at several processing points in the NASA WRS.

MATERIALS AND METHODS

Anhydrous isopropanol (99.5%), acetone (HPLC) and Degussa P25 TiO_2 (0.3 to 3.0 g/L) were used. Solutions (100 ppm) prepared freshly in nanopure water and gently shaken were stirred with the photocatalyst to ensure homogeneity. The pH values were between 3.02 and 10.72 (adjusted with HNO_3 and NaOH). $NaClO_4$ was used to adjust solution ionic strength. Experiments were carried out in small quartz tubes (25 mL) to minimize headspace. Samples were placed in ACE photochemical reactor equipped with ACE 450 watt mercury vapor lamp as a light source. Aqueous samples were filtered through hydrophilic polyethersulfone membrane using stainless steel syringe type holders. Shimadzu GC/FID equipped with EPG column was used for isopropanol and acetone analysis.

RESULTS AND DISCUSSION

Dark adsorption isotherms

Dark adsorption isotherms of isopropanol and acetone onto the surface of TiO_2 powder were performed at room temperature. Samples (100 ppm) were mixed with 2.0 g/L of TiO_2 and sealed. Tubes were then placed on a shaker in the incubator for 28 hr. The results in Figures (1 and 2) indicated that both isopropanol and acetone do not strongly adsorb to the surface of the photocatalyst (TiO_2). Such compounds prefer the bulk solution of the photocatalyst suspension rather than the surface.

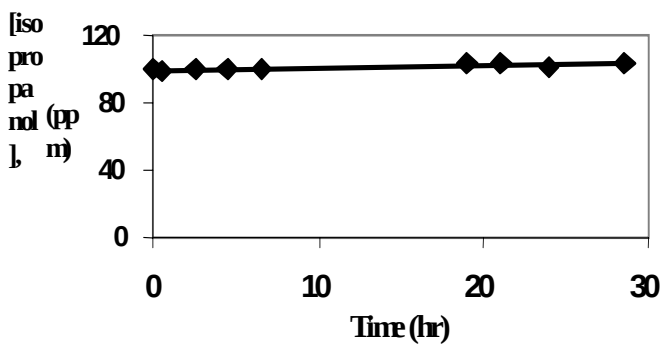

Figure 1. Dark adsorption of 100 ppm isopropanol onto 2.0 g/L TiO_2 at pH 4.6

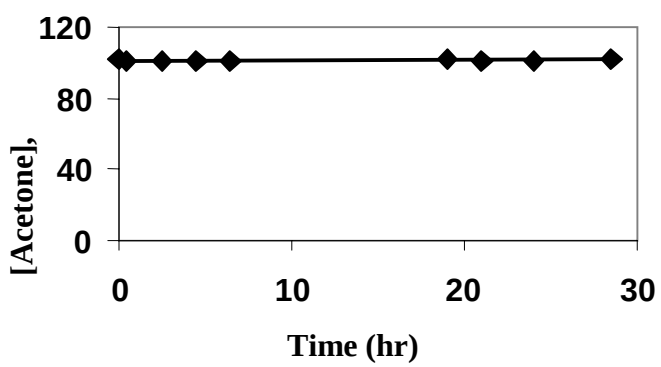

Figure 2. Dark adsorption of 100 ppm acetone onto 2.0 g/L TiO_2 at pH 4.6

Effect of TiO_2 concentration

Aqueous solutions of isopropanol (100 ppm) were irradiated with the UV light in the presence of different quantities (0.3 to 3.0g/L) of TiO_2 to investigate the optimum concentration of the photocatalyst. It was found that the degradation of isopropanol followed first-order kinetics. The degradation rate constants increased by increasing the concentration of TiO_2 up to 1.0 g/L as shown in Figure 3. It was noticed that rates were not significantly different for a two-fold increase in the photocatalyst level from 1.0 to 2.0 g/L. However, increasing the concentration of TiO_2 up to 3.0 g/L resulted in decrease the degradation rates of isopropanol.

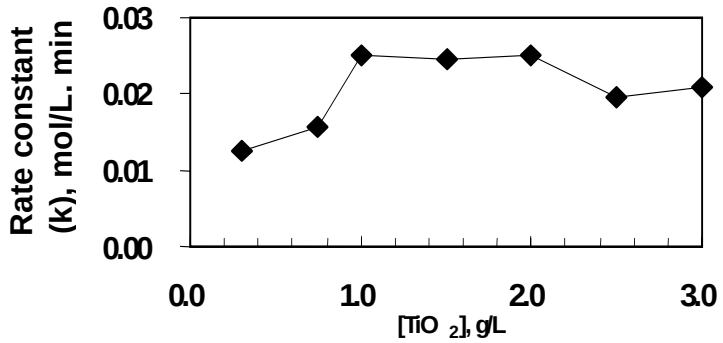

Figure 3. Degradation first-order rate constant (k) of isopropanol as a function of TiO_2 level

This observation can be explained by increase the degradation rate with increasing TiO_2 levels as the total number of the active sites provided by the photocatalyst increased. While at higher TiO_2 concentrations the degradation rate decreased as light attenuation affects increased[4,5]. However, increasing the level of the photocatalyst in the solution above 1.0 to 2.0 g/L did not affect the degradation rates and may be due to the steady state production of the hydroxyl radicals at that concentration.

Therefore, in all further experiments the TiO_2 concentrations was maintained at 2g/L which led to complete mineralization of both isopropanol and acetone in less than 6 hr as shown in Figure 4.

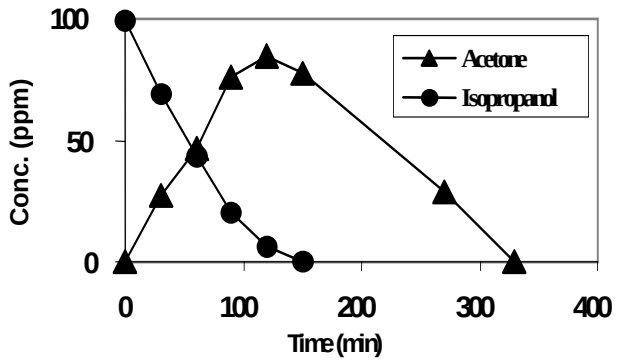

Figure 4. Photocatalytic degradation of isopropanol and its degradation product acetone with (2.0 g/L) TiO_2

Effect of ionic strength

Solutions with different ionic strengths ($1x10^{-4}$ to $1x10^{-1}$ M $NaClO_4$) were used to study the effect of ionic strength on the degradation rate. Results in Figure 5 indicated that increasing solution ionic strength up to $1x10^{-1}$ slightly enhanced the degradation of isopropanol. Although, increasing ionic strength decreases the adsorption capacity onto the surface of the photocatalyst[6] which must affect the degradation rate of the adsorbed substrate that reacts mainly with the adsorbed $^{\bullet}OH$ radicals. Increasing the ionic strength four orders of magnitude (from 10^{-4} to 10^{-1} M) did not significantly affect the degradation rate of isopropanol, supporting that the reaction is homogeneous in the bulk solution rather than on the surface of the photocatalyst.

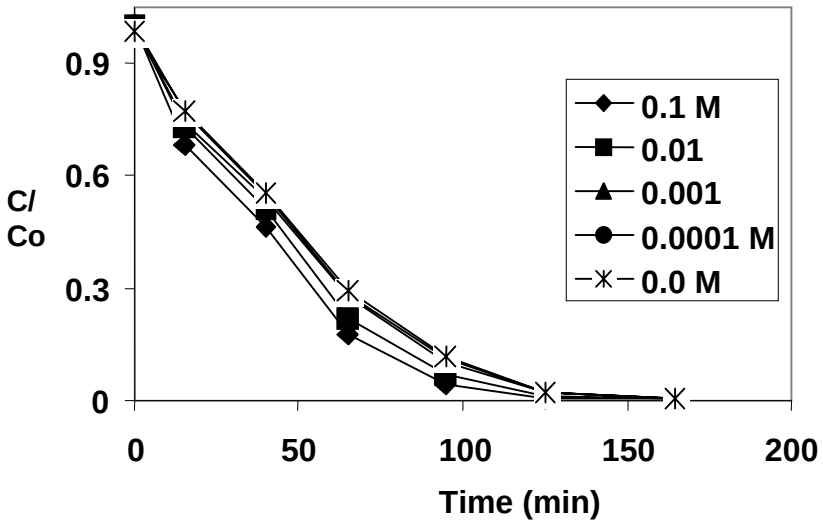

Figure 5. Effect of ionic strength ($NaClO_4$) on photodegradation of (100 ppm) isopropanol

Effect of tetranitromethane

Tetranitromethane (TNM) is a powerfull oxidizing agent which eliminates the species responsible for the formation of free $^{\bullet}OH$ radicals in the bulk solutions[7]. Experiment of photodegradation of isopropanol with 10^{-4} M TNM is shown in Figure 6. It was observed that presence of TNM in the solution decreased the degradation rate constant significantly from 85 to 59% over 75 min. Overall, we conclude that the results of TNM experiments combined with the minimal degree of adsorption of isopropanol and acetone onto the surface of the photocatalyst and the effect of ionic strength suggested that the photodegradation pathway occurs *via* free $^{\bullet}OH$ radicals in bulk solution rather than on the catalyst surface.

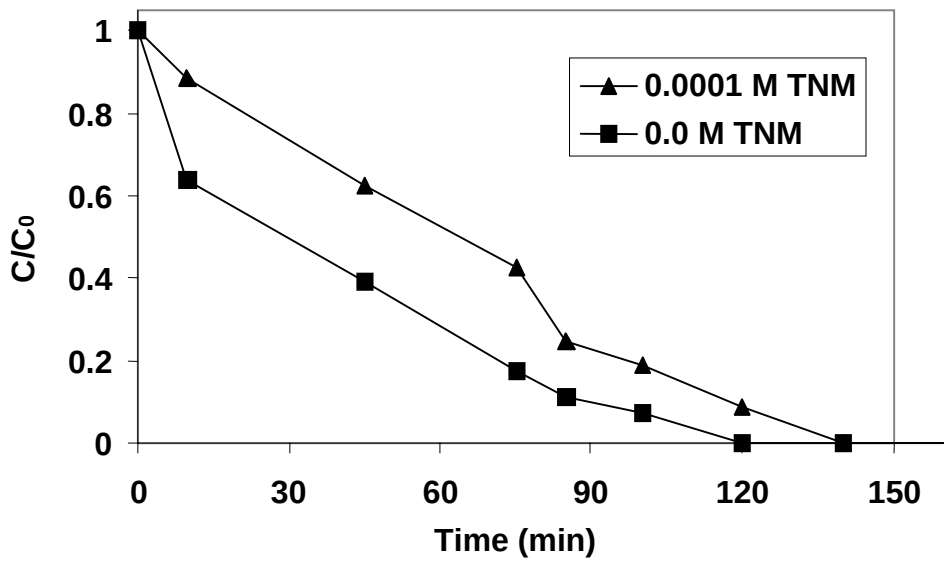

Figure 6. Effect of tetranitromethane (TNM) on the photodegradation of (100 ppm) isopropanol with 2g/L TiO_2

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