

**ADSORPTION AND PHOTOCATALYTIC DEGRADATION OF AQUEOUS SOLUTION OF POLAR ORGANIC POLLUTANTS**

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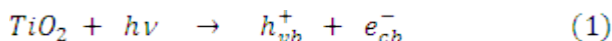
**Abstract**

This study examines the adsorption and the photodegradation of isopropanol and its degradation intermediate, acetone, as a polar organic pollutant. Both isopropanol (100 mg/L) and formed acetone are shown to be effectively photodegraded in aqueous suspensions of 2g/L TiO<sub>2</sub>. It was found that dark adsorption isothermal of isopropanol on the surface of TiO<sub>2</sub> was unfavoured process, which suggesting that the photodegradation reaction occurred in the bulk solution (homogeneous) rather than on the surface (heterogeneous) of the photocatalyst. In addition, homogeneous reaction is further confirmed by the decrease of the degradation rate of isopropanol in presence of 1x10<sup>-4</sup> M tetranitromethane (TNM) which is effectively eliminating the formation of free OH<sup>•</sup> radicals in the bulk solution. Under the studied conditions, the parent isopropanol and its degradation product, acetone, were completely degraded from aqueous solution in about 2.5 -5.5 h.

**Keywords:** *Isopropanol, Acetone, Photocatalytic degradation, TiO<sub>2</sub>, Polar organic compounds, Adsorption*

**Introduction**

In recent years aqueous suspensions of the photocatalyst TiO<sub>2</sub> is a well-established technique for the degradation of many environmental pollutants [1-3]. In this process, the UV irradiation of TiO<sub>2</sub> excites valence band electrons into higher conduction band energy levels leaving behind a hole in valence band (Eq.1).



The conduction band electrons (e<sup>-</sup><sub>cb</sub>) are capable of electron donation and reduce chemicals. Also, valence band holes (h<sup>+</sup><sub>vb</sub>) created by the promotion of the valence band electrons, are able to accept electrons from adsorbed oxidizable species. Therefore, both valence band holes (h<sup>+</sup><sub>vb</sub>) and conduction band electrons (e<sup>-</sup><sub>cb</sub>) are capable of initiating photo-reduction and photo-oxidation reactions, respectively. The thermodynamic feasibility of such a redox reaction is determined by the reduction potentials of TiO<sub>2</sub> and adsorbed constituents [4-6]. Photocatalytic

degradation of water contaminated by non-polar organic compounds is significantly enhanced by the adsorption of these compounds onto the surface of the photocatalyst. However, small polar organic compounds such as alcohols, ketones, and aldehydes are highly soluble and do not adsorb strongly to the  $\text{TiO}_2$  surface and therefore may be fairly resistant to photocatalytic degradation. Although many organic chemicals undergo photo-oxidation, photo-reduction reactions may occur depending on the redox properties of the chemical [7-9]. There has been much debate as to whether photoreactions occur on the surface of  $\text{TiO}_2$  or in the bulk solution. Several studies have demonstrated the significance of sorption of the organic compound on  $\text{TiO}_2$  surface [10]. The results of the adsorption process would be an evidence for determining if photodegradation of organic pollutant occurs by heterogeneous (surface-bonded OH radicals) or homogeneous (free OH radicals in bulk solution) reaction. The capacity of adsorbent for adsorbate (such as  $\text{TiO}_2$  for isopropanol) is obtained by adsorption isotherm model which is the equilibrium relationships between adsorbent/adsorbate systems. It is important to develop a model that can be used for the analysis of the equilibrium data [11-13]. The most frequently adsorption isotherm models are two classical adsorption models, i.e., Freundlich and Langmuir isotherms. In this study, the two models were used to describe the relationship between the amounts of isopropanol adsorbed on the surface of  $\text{TiO}_2$  at equilibrium.

The major objective of this study was to assess the potential of  $\text{TiO}_2$  suspensions to photodegrade a polar organic compound, isopropanol (ISP) and its degradation product acetone (ACE). This involved determination of the type of photoreaction through the adsorption process and the use of tetranitromethane.

## **Materials and Methods**

### **Chemicals**

Anhydrous isopropanol (99.5%), acetone (Aldrich) and Degussa P25  $\text{TiO}_2$  were used.  $\text{NaClO}_4$  (Fisher Scientific) was used to adjust solution ionic strength. All chemicals were used without further purification.

### **Dark adsorption isotherm**

Dark (isothermal) adsorption experiments of isopropanol (adsorbate) to the surface of  $\text{TiO}_2$  (adsorbent) were carried out by adding different portions of  $\text{TiO}_2$  (0.15, 0.30, 0.50, 0.75 and 1.00 g) to a series of a cylindrical cap-sealed quartz tubes

(25 mL) filled with a fixed concentration of isopropanol (100 mg/L) at natural pH. Tubes were then placed on a shaker in the incubator at room temperature. Control tube was prepared in the same manner without the addition of TiO<sub>2</sub>. Then the tubes were removed at different time integrals and the final concentration of isopropanol was determined using gas chromatography (GC/FID). The amount of isopropanol adsorbed at equilibrium  $q_e$  (mg/g) was calculated from the following equation:

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (2)$$

where  $C_0$ , and  $C_e$  are the initial concentration and equilibrium concentrations of isopropanol solution (mg/L), respectively, V is the total volume of isopropanol solution used (L), and W is the mass of TiO<sub>2</sub> (g). Two common isotherm models such as Freundlich and Langmuir were used to test the adsorption data.

**Freundlich isotherm**

Freundlich (1909) isotherm is an empirical equation describing mathematically the behavior of adsorbate (isopropanol) molecules on the surface of adsorbent (TiO<sub>2</sub>) at a constant temperature [14-15] as shown in the following equation:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where ,  $q_e$  is the amount of adsorbed (isopropanol) at equilibrium,  $C_e$  is the equilibrium solution concentration of isopropanol,  $K_F$  (mg/g (L/mg)<sup>1/n</sup>) is an indicator of the adsorption capacity and  $1/n$  is the adsorption intensity and indicates both the relative distribution of energy and the heterogeneity of the adsorbent sites. The constants  $K_F$  and  $1/n$  are determined experimentally as the intercept and the slope respectively of the linear form of the Freundlich model as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

**Langmuir isotherm**

Langmuir equation [16-18] is valid for monolayer sorption on to a surface with finite number identical sites. The non linear form of Langmuir isotherm can be written as

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where  $q_m$  is the maximum monolayer saturation capacity of adsorption (mg/g) and  $K_L$  is the Langmuir isotherm constant (L/mg) which is related to the affinity of the binding sites [19-20]. Both  $q_m$  and  $K_L$  will greatly impact the conclusions made about the experimental data.

The linear forms of Langmuir isotherm (Eq.6) is used to determine both  $q_m$  and  $K_L$  from the intercept and the slope respectively.

$$\frac{1}{q_s} = \frac{1}{q_m} + \frac{1}{q_m K_L} \left( \frac{1}{C_s} \right) \quad (6)$$

### Photocatalytic degradation experiments

Photocatalytic degradation experiments were performed on aqueous of (100 mg/L) isopropanol. All solutions of isopropanol were prepared freshly in nanopure water (18.1 M  $\Omega$  cm, Infinity™ ultrapure purification system). Experiments were carried out in a cylindrical cap-sealed quartz tubes (25 mL) to minimize headspace. The required amount of TiO<sub>2</sub> was added, and the solution was gently shaken and stirred for 15 min to ensure homogeneity. During the stirring procedure, the solutions in quartz tubes were shielded from light by aluminum foil. The pH values (measured with Orion digital pH meter) were 4.51 (natural solution pH without adjustment). Samples were placed in double-walled quartz ACE photochemical reactor equipped with ACE 450 watt medium pressure mercury vapor lamp as a light source. A cooling water jacket was used to maintain the temperature between 25 and 27°C.

### Analytical procedure

In both the adsorption and photocatalytic degradation experiments, aqueous samples were taken at regular time intervals. Then samples were taken and filtered through hydrophilic polyethersulfone membrane using stainless steel syringe type holders (Fisher Scientific). The concentrations of isopropanol and its photocatalytic degradation product (acetone) were determined using a Shimadzu (GC-17A) gas chromatography/flame ionization detector (GC/FID) equipped with fused silica capillary column (PEG stationary phase; 30 m length x 0.32 mm i.d. x 1.0  $\mu$ m film thickness, Aldrich). Samples (1  $\mu$ L) were injected at 200°C for both the injector and detector. Helium gas was using as a carrier gas (5 ml/min). Oven temperature was adjusted at 60°C for 2 min, then ramped to 80°C at 5°C /min. Split mode was selected

at 15:1. Calibration curves for isopropanol and acetone were prepared from their stock solutions and treated in the same manner. Duplicate samples were used for analysis.

**Results and discussion**

**Isotherms for the Sorption of isopropanol onto TiO<sub>2</sub> surface**

Adsorption of organic pollutants on to the photocatalyst would lead to enhancing the photocatalytic degradation process by adsorbed ·OH radicals [6, 21-22]. Thus it is significant to study dark adsorption of isopropanol on to TiO<sub>2</sub> surface before performing the photocatalysis experiments. To test the validity of adsorption and to provide information on the capacity of TiO<sub>2</sub> surface for isopropanol, different common isotherm models such as Freundlich and Langmuir [23-25] have been tested. In this study the best fitting isotherm has been determined by linear regression method.

The adsorption data were analyzed according to the linear form of both Freundlich (Eq. 3) and Langmuir isotherm (Eq.5). According to Freundlich equation, the plot of

$\log q_e$  versus  $\log C_e$  as shown in Fig.1, should lead to a straight line. As discussed previously, the constants  $K_F$  (indicator of the adsorption capacity) and  $1/n$  (the adsorption intensity) are determined from the intercept and the slope of that straight line, respectively. In addition, the plot of  $\frac{1}{q_e}$  versus  $\frac{1}{C_e}$  would also give a straight line

that allows to calculate  $q_m$  and  $K_L$  from the intercept and the slope respectively as

shown in Fig.2. The isotherm parameters ( $R^2$ ,  $n$ ,  $K_F$ ,  $q_m$  and  $K_L$ ) derived by regression analysis for Freundlich and Langmuir equations are shown in Table 1. The results in both Fig.1 and Fig.2 indicated that, there is a large deviation from the two fitted equations as indicated by the low values of the coefficient of determination ( $R^2$ ) which are 0.885, 0.908 for Freundlich and Langmuir respectively. According to Freundlich isotherm, the adsorption process is favoured when the value of the adsorption intensity ( $n$ ) in the range of 1-10 [26]. The results shown that the values of ( $n$ ) is less than 1 (0.014) and adsorption capacity ( $K_F$ ) of isopropanol onto TiO<sub>2</sub> surface is negligible as  $8.13 \times 10^{-140}$  (mg/g (L/mg)<sup>1/n</sup>). On the other hand, the value of

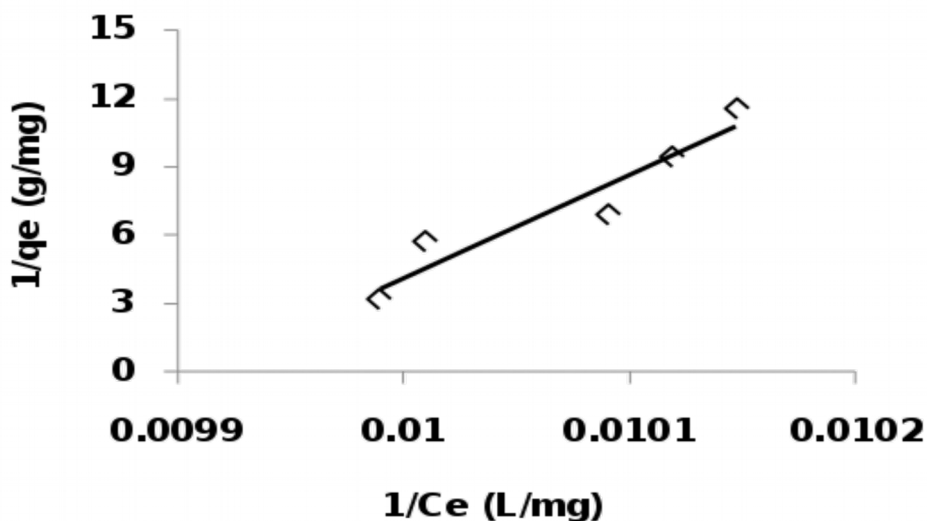
$q_m$  is the measure of the maximum amount of the adsorbate onto the surface of the adsorbent. Thus the adsorption process is favoured by the studied adsorbent when the value of  $q_m$  is quit high ( $\gg 1$ ) which indicates a strong electrostatic force of

attraction. The results in Table 1 indicated that the value of  $q_m$  of isopropanol onto  $TiO_2$  surface is negative value (- 0.002 mg/g). Also, the affinity of the binding sites on  $TiO_2$  surface for isopropanol ( $K_L$ ) resulted in negative value of -0.0099.

Further, Fig. 3 shows plot comparing the theoretical Freundlich and Langmuir isotherm equations with experimental data (by applying the isotherm constants obtained from both Freundlich and Langmuir equations as shown in Table1). The results indicated that the presence of the large deviation from the two fitted equations confirming that the data are not following any of these two common isotherm models.

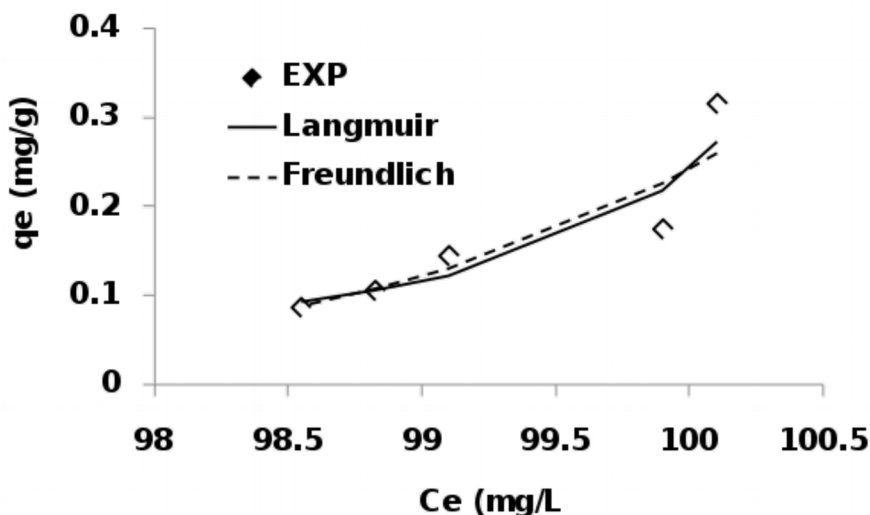
**Table 1: Isotherms for adsorption of isopropanol onto  $TiO_2$**

Isotherm	$T$ (K)	298
Langmuir-2	$q_m$ (mg/g)	-0.002
	$K_L$ ( $dm^3/mg$ )	-0.0099
	$r^2$	0.908
	$\Delta G^\circ$ (kJ/mol)	-10.6
Freundlich	$n$	0.014
	$K_F$ (mg/g)( $dm^3/mg$ ) $^{1/n}$	8.13E-140
	$r^2$	0.8846



**Fig. 2. Langmuir isotherm linear plot for the sorption of isopropanol on TiO<sub>2</sub> at temperature =25 °C, [isopropanol] = 100 mg/L and pH 4.5.**

Based on the above adsorption isotherm data, and the negative values of both the adsorption capacity and the affinity of the binding sites, it can be concluded that the adsorption of isopropanol onto the surface of TiO<sub>2</sub> is unfavorable process. Thus isopropanol as a polar organic pollutant and its degradation products would present mainly in the aqueous phase during the photocatalytic degradation process.



**Fig. 3: Freundlich and Langmuir isotherm equation plot for the adsorption of isopropanol on TiO<sub>2</sub> at temperature =25 °C, [isopropanol] = 100 mg/L and pH 4.5.**

### Photocatalytic degradation

#### Photocatalytic degradation of isopropanol

Experimental results of irradiation of (100 mg/L) isopropanol solution in the absence and presence of TiO<sub>2</sub> is shown in Fig. 4. It is indicated that direct photolysis (irradiation in the absence of TiO<sub>2</sub>) was found to have no measurable effect on the photodegradation of isopropanol. However, generation of a non-selective and powerful oxidant, 'OH radicals [27] by exciting of added TiO<sub>2</sub> in presence of UV light (Eq.1) significantly enhanced the degradation of isopropanol, since almost complete disappearance (ISP + 'OH → products) was obtained. Further, disappearance of the parent isopropanol resulted in the appearance of another intermediate. At the same time as, the concentration of isopropanol reached the lowest value at 6.25 mg/L, the

concentration of the intermediate reached the highest value at 84.82 mg/L at a photoperiod of 120 min.

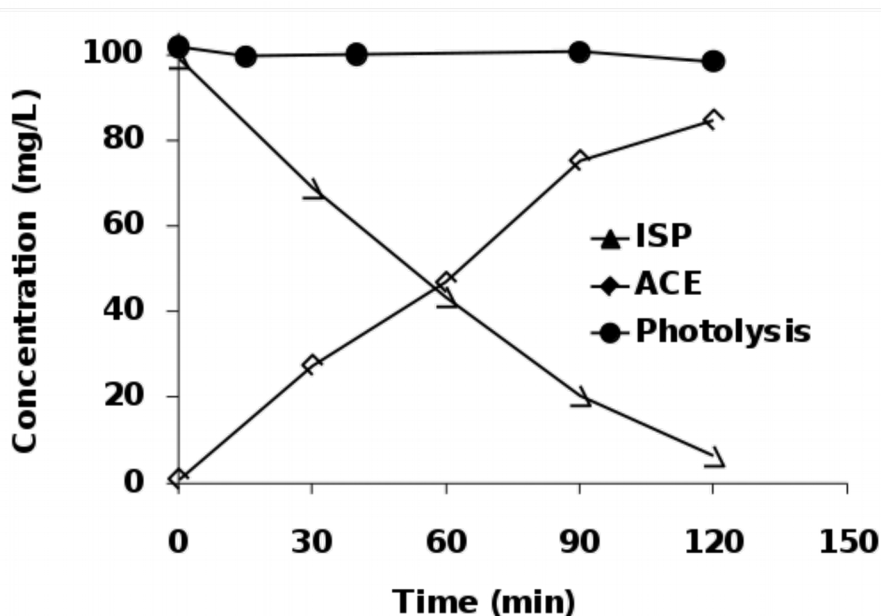
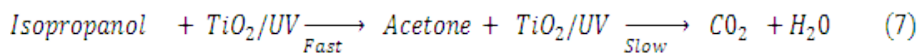


Fig.4: Photocatalytic degradation of isopropanol and formation of acetone as an intermediate under the conditions: [isopropanol] = 100 mg/L, pH = 4.51 and  $\text{TiO}_2$  = 2.0 g/L

#### Identification of the photodegradation products

As discussed previously, photocatalytic degradation of isopropanol leads to the formation of an intermediate. It was expected that the intermediate could be an acetone. The photocatalytic degradation of isopropanol in the presence of  $\text{TiO}_2$  may undergo the following reaction;



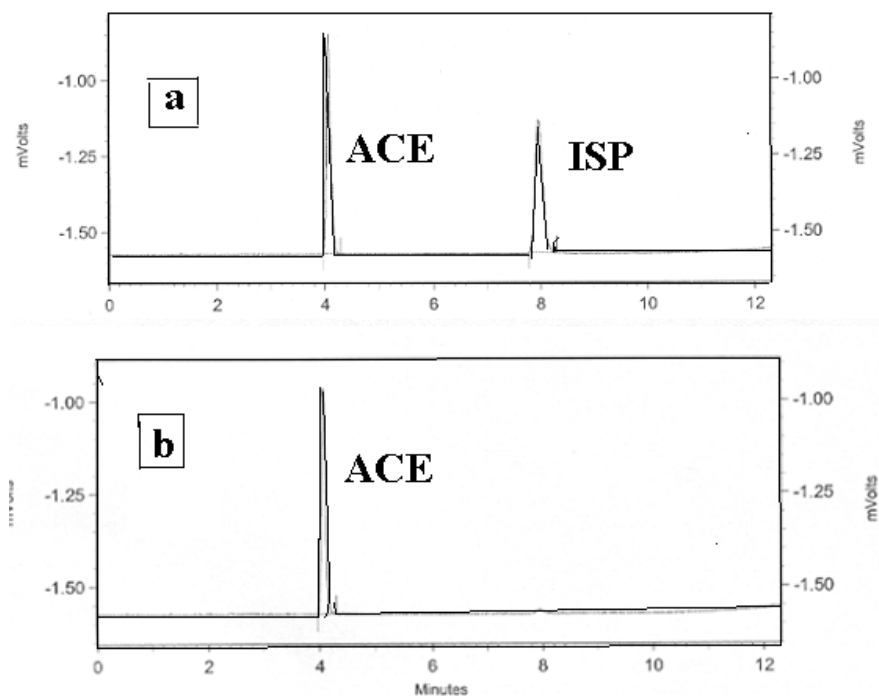
To confirm the intermediate under the studied conditions, a set of experiments were performed and samples were analyzed with the gas chromatography (GC/FID). Standard solutions of both isopropanol and acetone (100 mg/L) were injected in gas chromatography to determine their retention times before photodegradation experiments (Fig.5a). The results indicated that standard isopropanol appeared at 7.9 min, while standard acetone appeared at 4.0 min. During photocatalytic degradation



of isopropanol, the concentration of isopropanol decreased gradually and the only peak appeared was in the same retention time (4.0 min) of the standard acetone as shown in Fig. 5b (one run as an example). The results of the gas chromatography analysis (GC/FID) confirmed that the photodegradation product of photocatalytic degradation of isopropanol under the studied conditions is acetone. It should be noted that other intermediates such as carbonate ions and other organic acids (which could not be detected by GC/FID) may be formed during the photocatalytic degradation as indicated by the difference between the original concentration of isopropanol and the amount of formed acetone. Also, presence of carbonate ions could inhibit the degradation as formed acetone takes longer time to degrade.

#### **Heterogeneous vs. Homogeneous Oxidation.**

As reported in the literature [27] when  $\text{TiO}_2$  is excited with UV light of wavelengths less than 380 nm it produces valence band holes ( $h_{vb}^+$ ) and conduction band electrons ( $e_{cb}^-$ ) according to Eq. 1. Both  $h_{vb}^+$  and  $e_{cb}^-$  are capable for direct photooxidation and photoreduction of organic chemicals. Also, indirect photooxidation and photoreduction reactions occur by trapping both  $h_{vb}^+$  and  $e_{cb}^-$  by adsorbed  $\text{OH}^-$  ions and dissolved  $\text{O}_2$  respectively. Superoxide anion radical ( $\text{O}_2^{\bullet-}$ ) is formed when conduction band electrons ( $e_{cb}$ ) trapped by dissolved oxygen. While valence band hole ( $h_{vb}^+$ ) trapped by adsorbed  $\text{OH}^-$  ions (Eq 8) and form surface-bound hydroxyl radicals ( $\text{OH}_{ads}^{\bullet}$ ).



**Fig. 5: Total ion chromatogram of standard solutions of isopropanol (ISP) and acetone (ACE) before photodegradation (a) and total ion chromatogram of formed acetone as an intermediate in the presence of  $\text{TiO}_2$ /UV light (b), under the conditions: [isopropanol] = 100 mg/L, pH = 4.51 and  $\text{TiO}_2$  = 2.0 g/L**

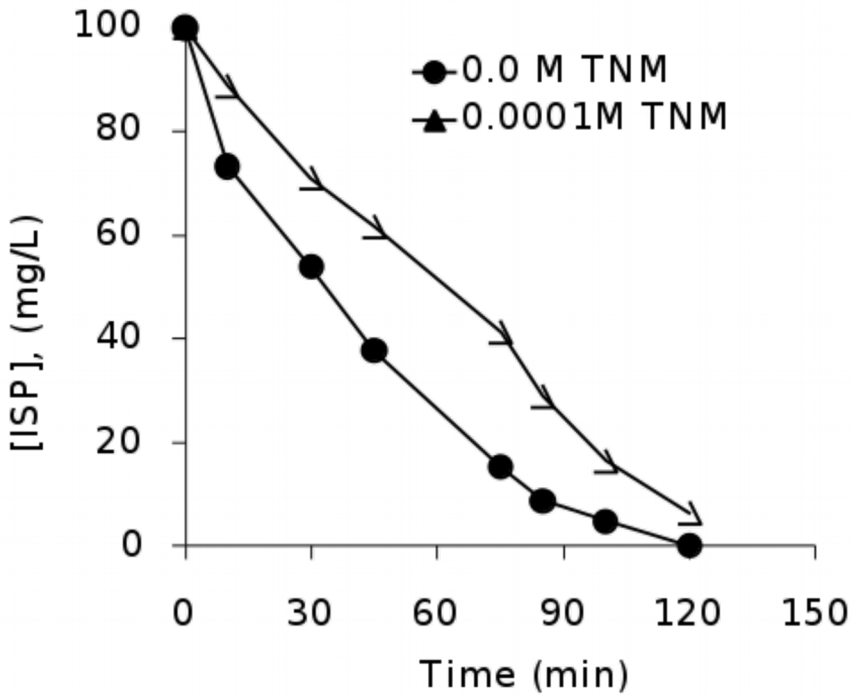
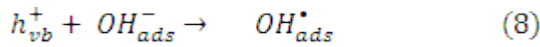
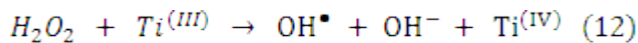
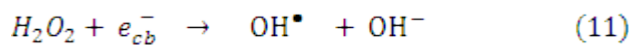
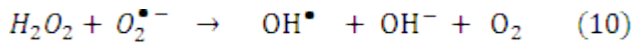
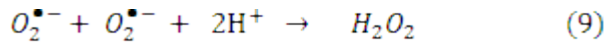


Fig.6: Effect of  $1 \times 10^{-4}$  M tetranitromethane (TNM) on the photodegradation of isopropanol under the conditions: [isopropanol] = 100 mg/L, pH = 4.51 and  $TiO_2 = 2.0$  g/L



This radical may stay adsorbed on the surface of the photocatalyst or diffuse a way into the bulk solution and called free radicals ( $OH_{free}^\bullet$ ) [28]. Further, free radicals ( $OH_{free}^\bullet$ ) in the bulk solution may also produced by reduction of hydrogen peroxide which formed from a reaction involving the superoxide anion radical ( $O_2^{\bullet-}$ ) [29] as follows:



Heterogeneous photooxidation reaction takes place by surface-bound hydroxyl radicals ( $OH_{ads}^\bullet$ ) on the surface of the photocatalyst [6], while homogeneous

photooxidation reaction occurs by free ( $\text{OH}_{\text{free}}^{\bullet}$ ) radicals in the bulk of solution [21, 28]. There has been much debate as to whether photoreactions occur on the surface of  $\text{TiO}_2$  or in the bulk solution [6]. It was reported that adsorption of the organic chemical onto the surface of the photocatalyst supports surface reaction [30-31, 10]. Different experiments such as examining both the adsorption isotherm of isopropanol onto the surface of  $\text{TiO}_2$  and the effect of tetranitromethane were used to determine if the photooxidation of isopropanol was a heterogeneous or homogeneous.

As discussed previously, based on the adsorption isotherm data, the adsorption of isopropanol onto the surface of  $\text{TiO}_2$  is unfavourable process which suggested that isopropanol and its degradation products would present mainly in the aqueous phase instead of the surface of  $\text{TiO}_2$  photocatalyst. Therefore, isopropanol and its degradation products should degrade mainly by the homogeneous  $\text{OH}^{\bullet}$  radicals ( $\text{OH}_{\text{free}}^{\bullet}$ ) which present in the bulk solution. Furthermore, it has been reported that tetranitromethane (TNM) is a powerful oxidizing agent used to remove the species responsible for the formation of free  $\text{OH}^{\bullet}$  radicals ( $\text{OH}_{\text{free}}^{\bullet}$ ) in solution [29]. Because TNM is not strongly adsorbed to the surface of  $\text{TiO}_2$  [6, 29], it will not remove adsorbed  $\text{OH}^{\bullet}$  radicals ( $\text{OH}_{\text{ads}}^{\bullet}$ ) from the surface of the photocatalyst. The results in Fig. 7 indicated that the rate of photodegradation of isopropanol significantly decreased in the presence of TNM. Because eliminating the the homogeneous  $\text{OH}^{\bullet}$  radicals ( $\text{OH}_{\text{free}}^{\bullet}$ ) by TNM, resulted in decrease the degradation of isopropanol. It is indicating that photodegradation of isopropanol involved homogeneous  $\text{OH}^{\bullet}$  radicals ( $\text{OH}_{\text{free}}^{\bullet}$ ) in the bulk solution rather than adsorbed  $\text{OH}^{\bullet}$  radicals ( $\text{OH}_{\text{ads}}^{\bullet}$ ) onto the surface of the photocatalyst.

### Mineralization of isopropanol

As discussed previously, gas chromatography (GC/FID) analysis showed disappearance in the peaks of isopropanol during the photodegradation process. The degradation of isopropanol was accompanied by the formation of acetone as confirmed by the appearance of one peak only on the chromatogram. Formation of one peak could be an evidence for the formation of only one organic compound as an intermediate. The other intermediates could not be detected by GC/FID which could be small polar organic acids and carbonate ions. Further, the results of photodegradation indicated that the parent isopropanol was completely degraded in less than 150 min in the presence of 2g/L  $\text{TiO}_2$  under the studied conditions as shown

in Fig.7. In addition, while the formed acetone degrades more slowly than the parent isopropanol, it was completely degraded in less than 6 hr.

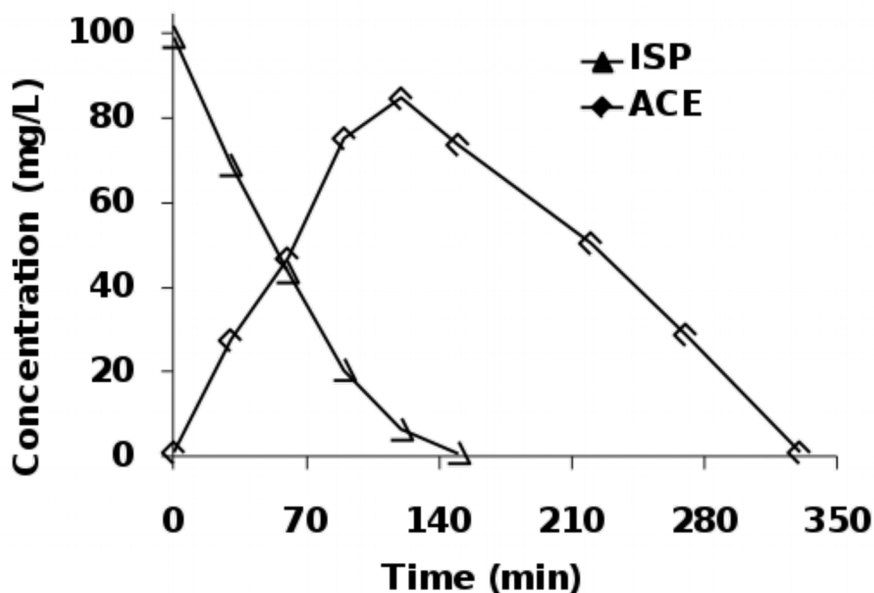


Fig.7: Mineralization of the parent isopropanol and the intermediate, acetone, under the conditions: [isopropanol] = 100 mg/L, pH = 4.51 and  $\text{TiO}_2$  = 2.0 g/L

### Conclusion

The results indicated that adsorption process of isopropanol and its degradation products on the surface of  $\text{TiO}_2$  is unfavourable. Homogeneous photodegradation process by free OH radicals in the bulk solution was the main process for photocatalytic degradation of isopropanol and acetone. Isopropanol mineralized in short time while acetone degraded in about than 5.5 hr.

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