

## EFFECTS OF PH ON ETHANOL PHOTOCATALYTIC OXIDATION USING $\text{TiO}_2$ AND ZEOLITE 13X AS CATALYST

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**Abstract.** Photocatalytic oxidation is a very beneficial technique used in the treatment of various organic pollutants. In this research, two of the most prominent catalysts,  $\text{TiO}_2$  and zeolite 13X were tested for their ability in optimising the photocatalytic oxidation of ethanol in aqueous solution in terms of ethanol adsorption and production of acetaldehyde as an intermediate for the reaction. Besides that, the effects of pH on the photocatalytic oxidation of ethanol in an aqueous solution by using  $\text{TiO}_2$  and zeolite 13X as catalysts were also determined. The experiments were conducted under UV irradiation with the presence of dissolved oxygen. Samples were taken every 40 minutes for 200 minutes of irradiation at different pH values (pH 3, pH 5, pH 7 and pH 9) and then analysed by HPLC. The findings of the experiments indicated that  $\text{TiO}_2$  was a better catalyst compared to zeolite 13X in terms of ethanol adsorption (i.e. adsorbs more ethanol) and the production of acetaldehyde as an intermediate product (i.e. produces less acetaldehyde). The results also indicated that the optimum level for photocatalytic oxidation of ethanol was in acidic condition. It was also found that the duration of irradiation plays a big role and shows tremendous effect to the photocatalytic oxidation of ethanol.

**Keywords:** Photocatalytic oxidation,  $\text{TiO}_2$ , zeolite 13X, ethanol adsorption, acetaldehyde production, pH values

**Abstrak.** Proses pengoksidaan fotomangkin adalah suatu teknik yang amat berguna dalam rawatan bahan pencemar organik. Dalam kajian ini, keberkesanan dua jenis mangkin iaitu,  $\text{TiO}_2$  dan zeolite 13X dalam mengoptimumkan proses pengoksidaan fotomangkin bagi etanol dalam fasa akueus diuji dari segi keberkesanan penyerapan etanol dan kuantiti asetaldehid yang dihasilkan sebagai produk perantara bagi tindakbalas fotomangkin ini. Selain itu, kesan pH ke atas proses pengoksidaan fotomangkin ini juga ditentukan. Eksperimen telah dijalankan di bawah sinar UV dengan kehadiran oksigen terlarut. Sampel-sampel dibuat setiap 40 minit untuk selama 200 minit di bawah pendedahan sinar UV pada berbagai pH berbeza (pH 3, pH 5, pH 7 dan pH 9). Sampel-sampel tersebut dianalisis menggunakan teknik HPLC. Hasil daripada uji kaji menunjukkan bahawa  $\text{TiO}_2$  mempunyai keberkesanan yang lebih tinggi berbanding zeolite 13X dari segi penyerapan etanol (iaitu menyerap lebih banyak etanol) dan dari segi penghasilan asetaldehid (iaitu menghasilkan kuantiti asetaldehid yang lebih rendah). Hasil kajian juga menunjukkan bahawa proses pengoksidaan fotomangkin bagi etanol mencapai tahap optimum dalam keadaan berasid. Begitu juga, hasil kajian mendapati jangkamasa pendedahan sistem fotomangkin kepada sinar UV memainkan peranan yang penting dan memberi kesan yang hebat terhadap proses pengoksidaan fotomangkin bagi etanol.

**Kata kunci:** Pengoksidaan fotomangkin,  $\text{TiO}_2$ , zeolite 13X, penyerapan etanol, penghasilan asetaldehid, nilai pH

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## 1.0 INTRODUCTION

In the production of chemical products, often, organic compounds would be involved commercially. Along the process, mainly in chemicals and petrochemicals industries, the waste water discharged could be contaminated with toxic organic residuals, which may be hazardous to the environment and could disturb the water quality once the effluent flows into the river and other waterways [1].

Environmental pollution, especially water pollution is one of the most feared problems to the modern societies. Since, waste treatment needs high-energy consumptions and produces toxic liquid and solid side yield [2], alternative treatment process that consumes less energy and produces non-toxic side products has to be discovered. Thus, photocatalytic oxidation (PCO) is viewed as an attractive option to be the alternative. PCO is an oxidation process that could stimulate chemical reaction with the help from certain catalysts in the presence of UV radiation.

Semiconductors such as  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{ZnS}$ ,  $\text{CdS}$  and  $\text{WO}_3$  have been known to possess photocatalytic character. Among them, titanium dioxide ( $\text{TiO}_2$ ) is the most widely use as inorganic catalyst for photocatalytic oxidation process, more for its activeness, great stability and non-toxic character. The photocatalyst, titanium dioxide, is a wide bandgap (3.2 eV) semiconductor, corresponding to radiation in the near UV range. Upon the absorption of this UV energy,  $\text{TiO}_2$  particles will form a paired electron ( $e^-$ ) and hole ( $h^+$ ), in the conduction band and valence band. The positive hole is apparently able to oxidize a water molecule to hydroxyl radical. The hydroxyl radical, in turn, is a powerful oxidant. The oxidation of organic contaminants seems to be mediated by a series of reactions initiated by hydroxyl radical on the  $\text{TiO}_2$  surface. For the photo-oxidation reaction to occur, both  $\text{TiO}_2$  and a UV light source are necessary [3].

Besides  $\text{TiO}_2$ , molecular sieves, or better known as zeolites are also known as remarkable catalysts. The most known type is the zeolite 13X. Having pore size of about 10 Å, zeolite 13X can adsorb any molecule smaller than 10 Å, be mainly used as catalyse carrier, co-adsorption of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ , as desiccant for medical and air compressor system, and can also be adjusted to fit other various applications [4].

PCO has great potential applications for the complete oxidation of organic pollutants, such as ethanol in dilute systems. Organics can be oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at room temperature on semiconductor catalysts in the presence of UV or near-UV illumination. The UV light excites electrons from the valence level to the conduction band of the semiconductor catalyst, leaving holes behind. The electron-hole pairs then can initiate redox reactions with surface species [5].

However, aqueous phase photocatalytic oxidation of ethanol to  $\text{CO}_2$  and water is thought to occur progressively via oxygenated intermediates, such as acetaldehyde and acetic acid:



while the second intermediate produced, acetic acid dissociates easily into  $\text{H}^+$  and  $\text{CH}_3\text{COO}^-$ , the acetaldehyde produced is hardly ionisable [6]. It is worth to note that exposure to acetaldehyde may results in toxic events such as irritation to the eyes and respiratory tract, nausea, headache, tiredness, and thirst [7].

In this study, the effectiveness of  $\text{TiO}_2$  and zeolite 13X on the photocatalytic oxidation of ethanol under certain pH condition will be studied.

## 2.0 METHODOLOGY

### 2.1 Materials and Apparatus

#### 2.1.1 Reagents

In this experiment, ethanol was used as a model reactant. The ethanol used was absolute ethanol, from HmbG Chemicals. This ethanol was then diluted to get the desired ethanol concentration. The  $\text{TiO}_2$  and zeolite 13X with average particle size of  $2\ \mu\text{m}$  used were supplied by Goodrich Chemical Enterprise (GCE) and Sigma-Aldrich Incorporated, respectively. Both catalysts were in powder form and were used without further purification. Acetic acid (0.2 M) and potassium hydroxide (0.2 M) were used in a small amount to control the pH of ethanol solution in order to achieve the desired pH value.

#### 2.1.2 Apparatus for Photocatalytic Oxidation

The apparatus used were a low intensity UV light to provide irradiation, two Mettler Toledo 320 pH meters to obtain the pH readings, two thermocouples to obtain the exact temperature of the samples, an air pump (240 Volts, 50 Hz) with split air tubes to supply the photocatalytic systems with oxygen, a Heidolph MR3003 Control hotplate and two magnetic stirrers, two 1000 mL beakers which acted as the photoreactors, a stopwatch and basic apparatus such as measuring cylinders, pipettes and volumetric flasks. A set of 20 mL sample bottles was used to collect and keep the samples before they were ready to be analysed.

### 2.2 Analyses

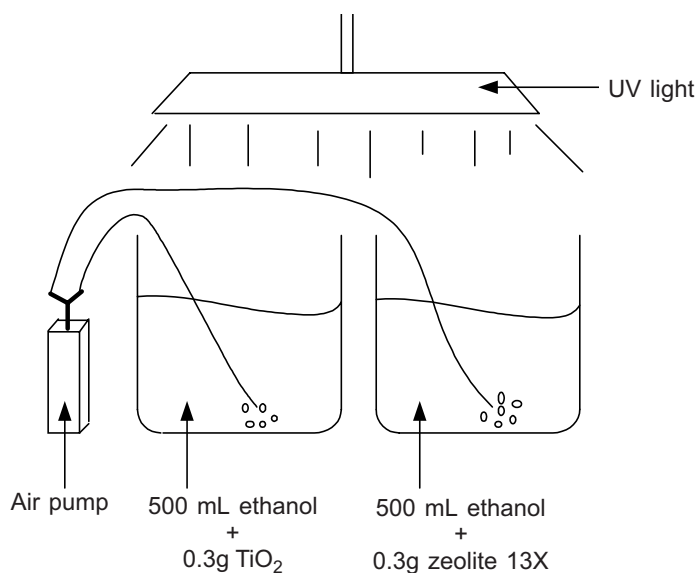
The adsorption of ethanol (decreasing in ethanol concentration) and the concentration of acetaldehyde produced as an intermediate were determined by an RI detector in a HPLC with  $\text{H}^+$  column (Aminex HPX-87H). 2.5 L of 0.005 M sulphuric acid was used as the mobile phase for the HPLC system.

### 2.3 Ethanol Preparation

Ethanol with initial concentration of 790 000 ppm was used. The dilution process and method were applied in order to obtain the desired ethanol concentration, which was 550 ppm used in this study.

### 2.5 Procedures

Two 1000 mL beakers (which acted as photoreactors) with 500 mL of diluted ethanol (550 ppm) each were added with 0.3 g of  $\text{TiO}_2$  and 0.3 g of zeolite 13X respectively. The solutions were then allowed to mix well by placing them on Heidolph stirrer at a speed of 500 rpm for 5 minutes each. The schematic diagram for photocatalytic oxidation of ethanol is shown in Figure 1.



**Figure 1** Schematic diagram for photocatalytic oxidation of ethanol

Oxygen was then supplied to both photocatalytic systems by using an air pump with split tubes. Both photocatalytic systems were then added with a few drops of acetic acid (0.2 M) or potassium hydroxide (0.2 M) to maintain the photocatalytic systems at pH 3. The temperatures of the systems were fixed at room temperature ( $\approx 26^\circ\text{C}$ ).

After obtaining the desired pH value (pH 3), UV light was switched on and a stopwatch was started. The pH values, temperatures and samples of both photocatalytic systems at  $t = 0$  minute, 40 minutes, 80 minutes, 120 minutes, 160 minutes and 200 minutes were taken. The same procedures as above were repeated for photocatalytic systems at pH 5, pH 7 and pH 9.

The samples were then kept in a refrigerator at 6-9°C to preserve their contents before they were analysed using HPLC to obtain the concentration of adsorbed ethanol and concentration of acetaldehyde produced as intermediates.

## 2.6 Determination of the Concentration of Ethanol Adsorbed and the Ratio of Acetaldehyde Produced Using HPLC Analysis

From the chromatogram obtained by analysing using HPLC, the concentration of ethanol adsorbed was calculated using an external standard method [8]. By applying the external standard method, concentration of ethanol in sample can be determined using Equation (1):

$$\text{Concentration}_{\text{unknown}} = \frac{\text{Area}_{\text{unknown}}}{\text{Area}_{\text{known}}} \times \text{Concentration}_{\text{known}} \quad (1)$$

where,

$\text{Concentration}_{\text{unknown}}$  = concentration of ethanol in a sample

$\text{Concentration}_{\text{known}}$  = concentration of ethanol in the blank sample for each experiment, which has been fixed the value at 550 ppm

$\text{Area}_{\text{unknown}}$  = Area of ethanol peak in a sample

$\text{Area}_{\text{known}}$  = Area of ethanol peak in the blank sample for each experiment

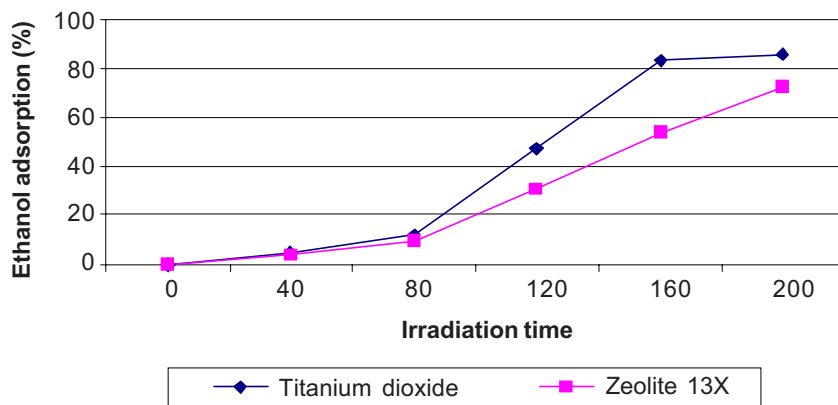
The concentration of acetaldehyde produced was very difficult to determine. This is because acetaldehyde initial concentration ( $\text{Concentration}_{\text{known}}$ ) is always zero. Therefore, the external standard method could not be applied. However, the trend of acetaldehyde produced can be determined by assuming that the area of acetaldehyde peak obtained from the chromatogram represents the quantity of acetaldehyde produced.

It was reported that the peak of ethanol usually can be detected by HPLC at retention time  $\approx 8 \pm 1$  minutes [9] while the peak of acetaldehyde usually detected at  $\approx 6.25 \pm 0.5$  minutes [7]. However, in this study, retention time detected for ethanol and acetaldehyde was at 5.967 and 8.667 minutes respectively.

## 3.0 RESULTS AND DISCUSSIONS

### 3.1 Photocatalytic Oxidation of Ethanol at pH 3

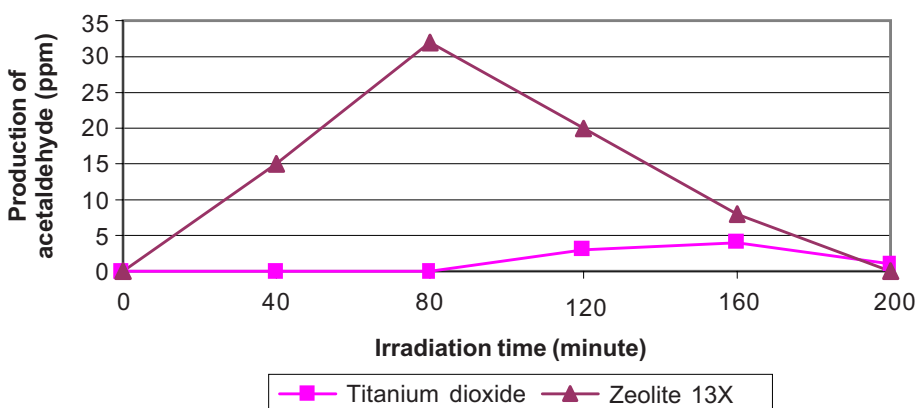
At pH 3, the  $\text{TiO}_2$  catalyst and zeolite 13X performed very well in adsorbing ethanol (Figure 2). At irradiation time between 0 to 80 minutes, the adsorptions of ethanol by both catalysts were equally the same. However, from 80 to 200 minutes,  $\text{TiO}_2$  adsorbed ethanol more rapidly compared to zeolite 13X. At the end of the experiment (after 200



**Figure 2** Percentage of ethanol adsorption using  $\text{TiO}_2$  and zeolite 13X as catalysts at pH 3

minutes irradiation), 85% of the initial ethanol was adsorbed on  $\text{TiO}_2$  surface while 72 % was adsorbed by zeolite 13X.

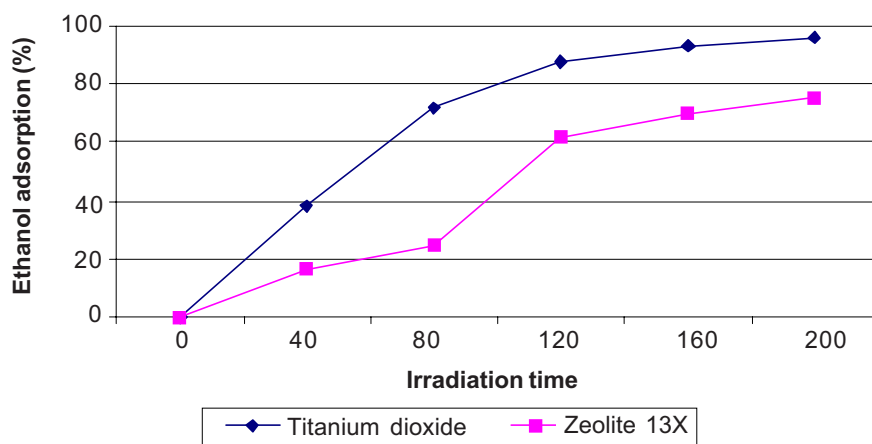
$\text{TiO}_2$  showed a near-constant low production of acetaldehyde intermediate throughout the experiment at pH 3 (Figure 3). There was zero production of acetaldehyde in the first 80 minutes of irradiation. After that, only a very small quantity of acetaldehyde could be traced and could be taken as zero production of acetaldehyde at the end of irradiation period. In contrast, zeolite 13X showed rapid production of acetaldehyde as started and reached maximum at minutes 80. The production then dropped immediately and reach zero acetaldehyde at the end of irradiation (200th minute).



**Figure 3** Production of acetaldehyde as intermediate product in photocatalytic oxidation of ethanol using  $\text{TiO}_2$  and zeolite 13X as catalysts at pH 3

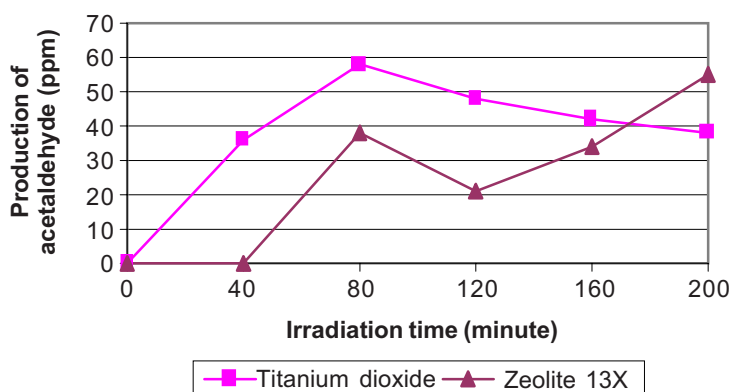
### 3.2 Photocatalytic Oxidation of Ethanol at pH 5

Figure 4 shows the adsorption of ethanol using  $\text{TiO}_2$  and zeolite 13X as catalysts at pH 5. Throughout the experiment (from 0 to 200 minutes of irradiation), ethanol adsorption was higher on  $\text{TiO}_2$  surface compared to zeolite 13X surface. This may be due to  $\text{TiO}_2$  exceptional ability to adsorb photons with energy equal or higher than its band gap energy ( $\lambda < 385 \text{ nm}$ ). The percentage of ethanol adsorption throughout the experiment is 96 % and 75 % using  $\text{TiO}_2$  and zeolite 13X respectively.



**Figure 4** Percentage of ethanol adsorption using  $\text{TiO}_2$  and zeolite 13X as catalysts at pH 5

From Figure 5, it is observed that at pH 5,  $\text{TiO}_2$  shows a rise in acetaldehyde production during the first 80 minutes of irradiation. After that, the quantity of acetaldehyde produced decreased slowly till the end of irradiation to the ratio of 40.

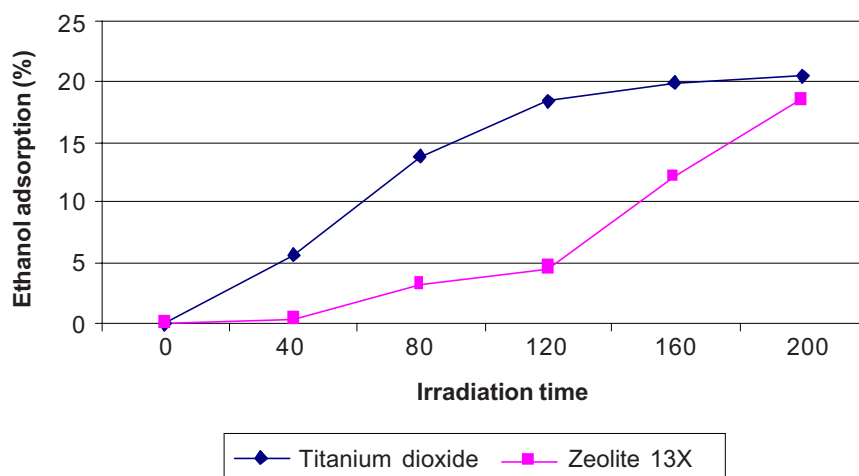


**Figure 5** Production of acetaldehyde as intermediate product in photocatalytic oxidation of ethanol using  $\text{TiO}_2$  and zeolite 13X as catalysts at pH 5

When using zeolite 13X as catalyst, there was no production of acetaldehyde at the first 40 minutes of irradiation. There was a sharp rise of acetaldehyde production 40 minutes later, but it dropped during irradiation of 80 to 120 minutes. However, after the irradiation of 120 minutes, the production of acetaldehyde rose very high, resulting in a large quantity of accumulated acetaldehyde at the end of the irradiation.

### 3.3 Photocatalytic Oxidation of Ethanol at pH 7

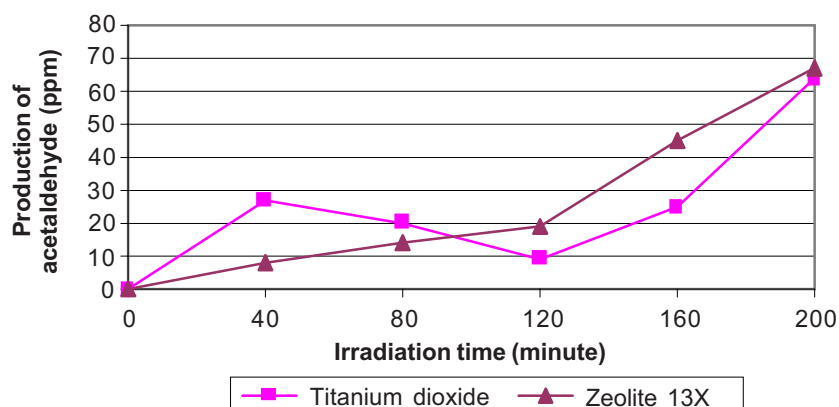
At pH 7 (neutral condition),  $\text{TiO}_2$  shows more adsorption during 80 to 160 minutes irradiation compared to the adsorption shown by zeolite 13X (Figure 6). However, the adsorption degree decrease and eventually after 200 minutes irradiation, both  $\text{TiO}_2$  and zeolite 13X show nearly equal adsorption of ethanol. The percentage of ethanol adsorption throughout the experiment is 21% using  $\text{TiO}_2$  as catalyst and 19% using zeolite 13X as catalyst. This percentages indicated that adsorption of ethanol are rather poor at pH 7 using both types of catalyst.



**Figure 6** Percentage of ethanol adsorption using  $\text{TiO}_2$  and zeolite 13X as catalysts at pH 7

Figure 7 indicates that at pH 7,  $\text{TiO}_2$  shows a quite high production of acetaldehyde from 0 to 40 minutes irradiation, but then it decreased during the irradiation time of 40 to 120 minutes and rised again after that until the end of irradiation. Zeolite 13X shows a smoother increment of acetaldehyde production. The mentioned intermediate's quantity rose in a faster rate during the final 80 minutes of irradiation.

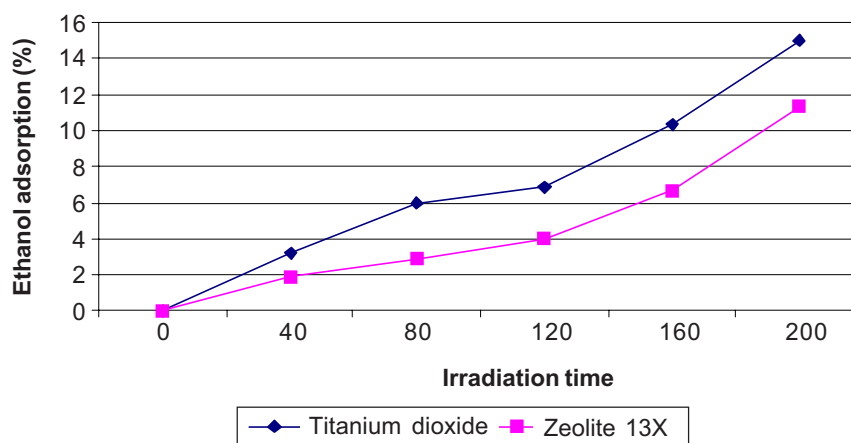




**Figure 7** Production of acetaldehyde as intermediate product in photocatalytic oxidation of ethanol using  $\text{TiO}_2$  and zeolite 13X as catalysts at pH 7

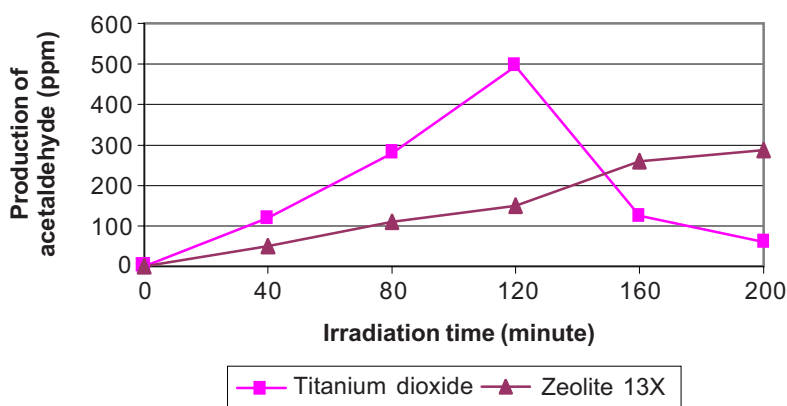
### 3.4 Photocatalytic Oxidation of Ethanol at pH 9

Figure 8 shows the adsorption of ethanol using catalysts  $\text{TiO}_2$  and zeolite 13X at pH 9. At pH 9,  $\text{TiO}_2$  and zeolite 13X both show nearly the same adsorption of ethanol throughout the experiment. It was also observed that the adsorptions of ethanol by both catalysts were seriously retarded at pH 9, which is alkaline condition. The percent of ethanol adsorption using  $\text{TiO}_2$  as catalyst is only 5 % while the ethanol adsorption percentage using zeolite 13X as catalyst is higher at 11%.



**Figure 8** Percentage of ethanol adsorption using  $\text{TiO}_2$  and zeolite 13X as catalysts at pH 9

As can be seen in the Figure 9, the production of acetaldehyde as intermediate product of the photocatalytic oxidation of ethanol using both mentioned catalysts was exceptionally high at pH 9, as it resulted into 3-digits ratio. During the 0 to 120 minutes irradiation, TiO<sub>2</sub> showed such a high increment in acetaldehyde accumulation. However, the acetaldehyde quantity reduced quite drastically in the final 80 minutes of irradiation, resulting in the ratio of 60 at the end of the experiment. The accumulation of acetaldehyde in the reaction using zeolite 13X as catalyst rose steadily throughout the experiment, resulting in the highest accumulation of acetaldehyde ever at the end of irradiation.



**Figure 9** Production of acetaldehyde as intermediate product in photocatalytic oxidation of ethanol using TiO<sub>2</sub> and zeolite 13X as catalysts at pH 9

From Figures 2, 4, 6 and 8, it can be said that TiO<sub>2</sub> shows a better performance in adsorbing ethanol compared to zeolite 13X. Besides that, it clearly indicates that both catalyst performed very well in adsorbing ethanol at lower pH (acidic condition) but their adsorption ability obviously decreased as the pH value increased to pH 7 (neutral condition) and keep on decreasing when the pH value increased to pH 9 (alkaline condition). The interpretation of pH effect on the photocatalytic process is very difficult because of its multiple roles such as electrostatic interactions between the semiconductors surface, solvent molecules, substrate and charged radicals formed during the reaction process. The ionisation state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions respectively, as shown in Equations (2-3):



The better efficiency for the degradation of compounds at lower pH may be due to the fact that orbital valence of the catalyst were activated in a high acceleration mode

and therefore, produced more protons and electrons. These protons react with hydroxyl ions (OH<sup>-</sup>) and produced radical hydroxide (OH<sup>•</sup>) [6]. Overall, the results indicate that the optimum pH in terms of ethanol adsorption using both catalysts is pH 5. It is also observed that the photocatalytic oxidation of ethanol increase with the increment of irradiation duration. This was physically evident especially during the running of the experiment at pH 3 and pH 5. This might be because as irradiation period increases, more oxygen and photons from the UV light were adsorbed on both catalysts surfaces.

Although TiO<sub>2</sub> exhibits a better performance in adsorbing ethanol, zeolite 13X also shows quite a remarkable performance in adsorbing ethanol. This may be due to zeolite 13X's large pore opening, which allows in adsorbing molecules up to 10 Å diameters. Zeolite 13X also has cation sites that have a strong affinity to a polar molecule [10]. TiO<sub>2</sub> also proves itself to be a more reliable catalyst compared to zeolite 13X as it accumulated lesser acetaldehyde, as shown in Figures 3, 5, 7 and 9. The results also exhibit less acetaldehyde at low pH value. It is suggested that CO<sub>2</sub> is produced at low pH while at pH value > 7, only very little mineralisation (CO<sub>2</sub> production) of ethanol was absorbed.

#### 4.0 CONCLUSIONS

From this study, it can be concluded that in terms of ethanol adsorption, TiO<sub>2</sub> shows a better performance in adsorbing ethanol compared to zeolite 13X at all the four tested pH values (pHs 3, 5, 7 and 9). Nonetheless zeolite 13X shows remarkable adsorption ability too, almost as good as TiO<sub>2</sub>. It was also observed that TiO<sub>2</sub> is a better catalyst compared to zeolite 13X in terms of the production of acetaldehyde (produces less acetaldehyde) as an intermediate of photocatalytic oxidation of ethanol. Photocatalytic oxidation of ethanol in an aerated aqueous system using TiO<sub>2</sub> and zeolite 13X as catalysts is strongly pH dependent. If pH is acidic, the oxidation of ethanol progresses very well but if the pH is alkaline, the oxidation process can be seriously retarded. The oxidation of ethanol is very poor at neutral condition (pH 7). Besides that, the duration of irradiation has some role in the efficiency of photocatalytic oxidation of ethanol in an aqueous system.

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