

Decomposition of aniline in aqueous solution by UV/TiO₂ process with applying bias potential

Young Ku*, Ping-Chin Chiu, Yiang-Chen Chou

Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei 106, Taiwan

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ABSTRACT

Application of bias potential to the photocatalytic decomposition of aniline in aqueous solution was studied under various solution pH, bias potentials and concentrations of potassium chloride. The decomposition of aniline by UV/TiO₂ process was found to be enhanced with the application of bias potential of lower voltages; however, the electrolysis of aniline became more dominant as the applying bias potential exceeding 1.0 V. Based on the experimental results and calculated synergetic factors, the application of bias potential improved the decomposition of aniline more noticeably in acidic solutions than that in alkaline solutions. Decomposition of aniline by UV/bias/TiO₂ process in alkaline solutions was increased to certain extent with the concentration of potassium chloride present in aqueous solution. Experimental results also indicated that the energy consumed by applying bias potential for aniline decomposition by UV/bias/TiO₂ process might be much lower than that consumed for increasing light intensity for photocatalysis.

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1. Introduction

Photocatalytic process using various semiconductors under appropriate UV illumination has been regarded as potential technology to decompose organic pollutants [1,2]. However, the decomposition efficiency is significantly hindered by the recombination of light-induced electron-hole pairs for most photocatalytic reactions. Recently, the application of bias potential to a photocatalytic process was considered to inhibit electron-hole recombination and to increase the photocatalytic efficiency. The mechanism of the bias-assisted photocatalytic process (also called photoelectrocatalytic (UV/bias/TiO₂ process) has been proposed by previous studies [3,4] and is illustrated in Fig. 1. The photocatalysts immobilized on conductive substrate act as photoanode in the UV/bias/TiO₂ process, while external anodic bias is provided by a potentialstat/galvanostat to drive the light-induced electrons toward cathode and to inhibit the recombination of electron and hole pairs [5].

Decomposition rate of 4-chlorophenol in aqueous solution was enhanced five-fold reported by Vinodgopal et al. with the application of bias potential of 0.6 V due to the anodic bias pulled the electrons away from the surface of TiO₂ to the cathode [6,7]. Wang et al. also found that the decomposition of 4-chlorophenol

by UV/bias/TiO₂ process in aqueous solution with the bias potential of 0.6 V was enhanced with increasing solution pH because more hydroxyl radicals were generated in alkaline solutions [8].

Kim and Anderson discussed the effect of the types of electrolyte for the decomposition of formic acid by photocatalytic and UV/bias/TiO₂ processes [9]. The addition of various electrolytes, including KCl, NaClO₄, NaNO₃, and Na₂SO₄, to aqueous solution caused the decrease of decomposition efficiency of formic acid by photocatalytic process due to the competitive adsorption between the formate and electrolytic ions on the TiO₂ surface. However, decomposition of formic acid was enhanced by the addition of KCl and NaNO₃ as the electrolytes in the UV/bias/TiO₂ process with the bias potential of 0.3 V. Chloride ions adsorbed on the active sites may react with positive holes to form free chlorine, Cl•, an oxidative agent to decompose formic acid in aqueous solution. The addition of NaCl as electrolyte exhibited higher decomposition efficiency than other electrolytes, such as NaClO₄, KNO₃ and Na₂SO₄, for treating remazol brilliant orange 3R (a reactive dye) by UV/bias/TiO₂ process [10].

Aniline is frequently used as a raw material in industries such as dye synthesis and drug production, and its molecular structure contains an amino group (–NH₂) on an aromatic ring. Aniline was selected to be the target pollutant in this study because its low decomposition efficiency by photocatalytic and photochemical treatment resulted from its low adsorbed quantity on the surface of TiO₂ in aqueous solutions [11]. The objective of this study is to investigate the enhancement of aniline decomposition by applying bias potential on UV/bias/TiO₂ process in aqueous solutions. The

* Corresponding author. Tel.: +886 2 27333141x7606; fax: +886 2 23785535.

E-mail addresses: ku508@mail.ntust.edu.tw, ku@ch.ntust.edu.tw, ku@mail.ntust.edu.tw (Y. Ku).

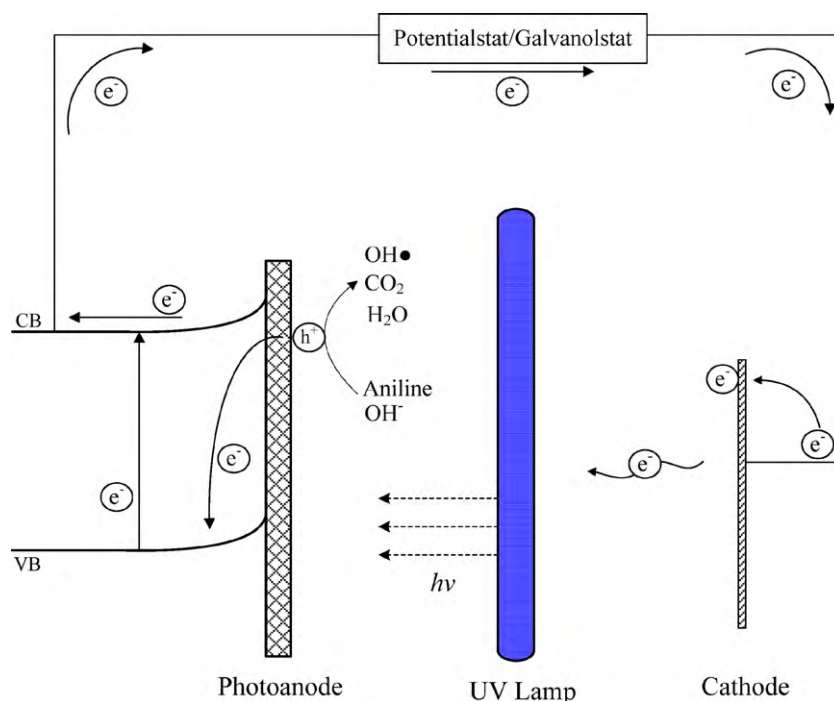


Fig. 1. Proposed mechanism of the PEC process.

effects of operational parameters, such as solution pH, electrolyte concentration and bias potential on aniline decomposition and calculated synergetic factors with the application of bias potential, were studied.

2. Experimental

Chemicals used in this study were analytical grade without further purification. The TiO_2 suspension was prepared by adding 10 g of Degussa P-25 TiO_2 in 150 mL of ethanol solution stirred by a magnetic stirrer for 30 min and sonicated for more than 6 h. A titanium plate (a width of 180 mm and a length of 100 mm) with 99.7% purity was etched by 6 M hydrochloric acid at 75°C for an hour and subsequently washed by acetone, ethanol and de-ionized water in order to remove the organics and particles from the surface of titanium plate. The titanium plate was then impregnated in the TiO_2 suspension for 1 min and pulled up slowly for several times and then dried at the room temperature. The TiO_2 coated titanium plate was then put into the muffle furnace for sintering at higher temperature (350 – 550°C) for 1 h to remove the residual ethanol on TiO_2 film.

The schematic diagram of the UV/bias/ TiO_2 reactor designed in this study is shown in Fig. 2. The UV/bias/ TiO_2 reactor was made of a Pyrex glass vessel of 1 L volume with a quartz tube housing a Sparkie FL10W/BLB mercury lamp with wavelength of 365 nm and approximately 10 W maximum output. The light intensity of mercury lamp was controlled by adjusting the variable voltage transformer and was detected by the ILT 1400 radiometer/photometer equipped with the SEL005 radiation sensor. For all of the experiments, $740 \mu\text{W}/\text{cm}^2$ of light intensity was applied. The TiO_2 -Ti plate, 304 stainless steel mesh and saturation calomel electrode were used as the photoanode, cathode and reference electrode, respectively, in the UV/bias/ TiO_2 reactor system. Aqueous solution containing 10 mg/L aniline was added into the reactor. An automatic titrator (Kyoto Electronics AT-400) was used to maintain the solution pH at a constant level during whole reaction course by dripping 1 M HCl or KOH solution. The application of 0–2.0 V bias potential on the photoanode was controlled by the EG&G Model 273

potentialstat/galvanostat for all of the experiments. The solutions were sampled at each intermittent period of reaction and measuring the concentration of aniline by a Spectra-Physics P1000 HPLC equipped with a Pursuit 5u C18 column ($250 \text{ mm} \times 4.6 \text{ mm}$) and a Spectra System UV 1000 detector by wavelength of 280 nm. The experiment would keep a constant bias potential for a few minutes and then started up reaction by UV irradiation.

3. Results and discussion

The photocatalytic decomposition efficiency of aniline using TiO_2 -Ti plates calcined from 350 to 550°C was decreased for experiments using TiO_2 -Ti plates calcined at higher temperatures. The decrease of decomposition efficiency resulted in the aggregation of TiO_2 particles during calcination process. The SEM images of

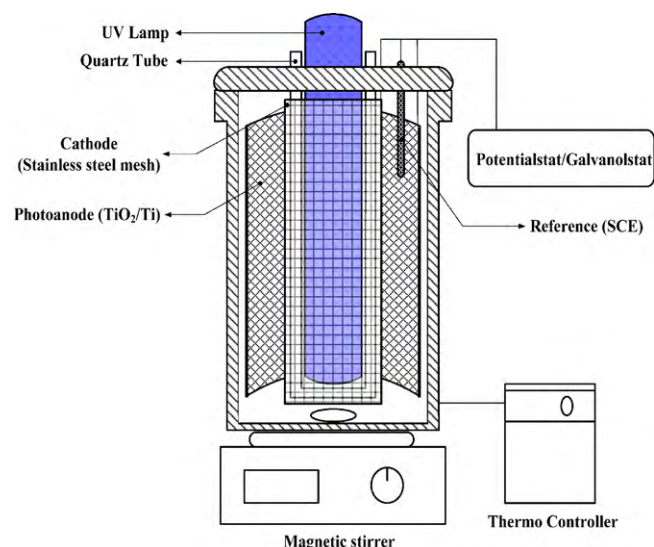


Fig. 2. Schematic diagram of the PEC reactor.

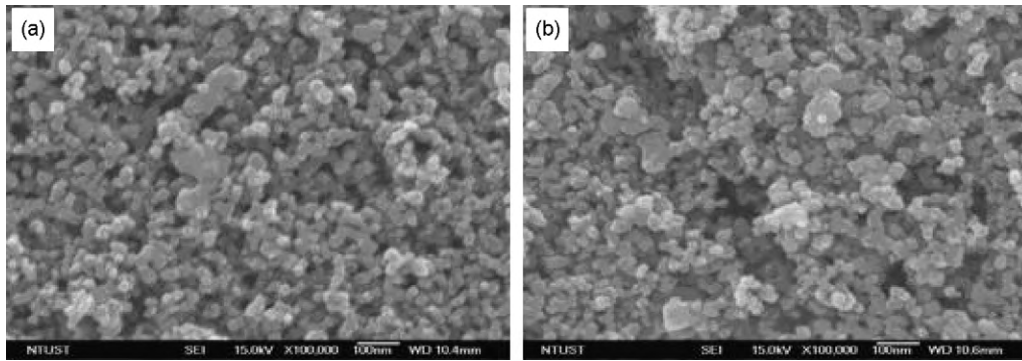


Fig. 3. Immobilized TiO₂ particles SEM images under calcination temperatures of (a) 350 °C and (b) 550 °C.

Fig. 3 illustrated that the particle size observed by SEM image was from 30–75 to 40–100 nm at calcination temperatures of 350 °C and 550 °C, respectively. From observation of SEM images, the surface area was assumed to decrease with increasing size of TiO₂ particles coated on titanium plate. To provide higher photocatalytic activity, the photoanodes calcined at 350 °C were used in the subsequent experiments.

Experiments to examine the effect of solution pH were conducted in aqueous solutions with pH varying from 3 to 11, and the results were shown in Fig. 4. Decomposition of aniline was increased with the increase of solution pH. Aniline decomposition for experiment conducted with solution pH 11 was approximately five-fold higher than that conducted with solution pH 3. Both aniline species and TiO₂ surface are negatively charged in alkaline solutions because the *pK_a* of aniline and zero point of charge (*Z_{pc}*) of TiO₂ were reported to be 4.65 and 6.30, respectively [11]. Therefore, the adsorption of aniline species on the surface of TiO₂ in alkaline solutions is assumed to be minimal because of charge repulsion. From the literature published by Kamble et al. illustrated that as solution pH increased from 3 to 12, the photocatalytic decomposition rate of aniline increased because higher concentration of hydroxyl radicals were generated [12]. Consequently, decomposition of aniline in alkaline solution was contributed by the hydroxyl radicals generated by the reactions between holes and OH⁻ or H₂O species described as follows [13]:

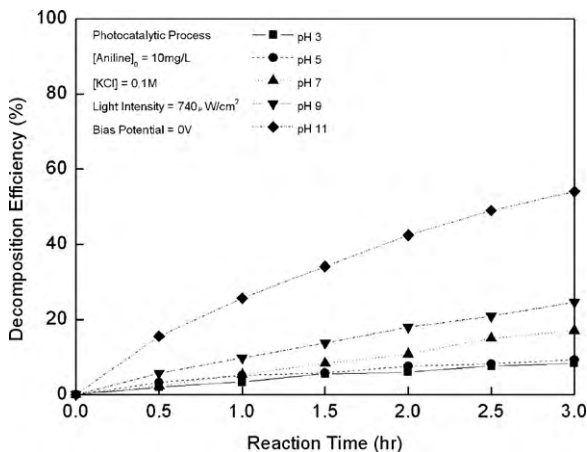


Fig. 4. Decomposition of aniline by UV/TiO₂ process in aqueous solutions of various pH.

As depicted in Fig. 5, no aniline decomposition by bias/TiO₂ process was observed for experiments conducted with applied bias potential less than 1.0 V; however, the decomposition of aniline was increased remarkably with increasing bias potential for experiments conducted with applied bias potential higher than 1.0 V. Decomposition of aniline by UV/bias/TiO₂ process for experiments conducted in alkaline solution of pH 11 was much higher than those conducted in acidic solution of pH 3. The effect of solution pH by conducting UV/bias/TiO₂ process published by Leng et al. was similar to the results of this study that the apparent rate constant increased by increasing solution pH from 4 to 12 as application of 0.5 V bias potential [14]. Combining the results from the literature and this study, bias potential applied on photoanode lower than 1.0 V did not vary the trend of decomposition efficiency of aniline. The enhancements of aniline decomposition by UV/bias/TiO₂ process using 1.0 V bias potential for experiments conducted in acidic and alkaline solutions were similar (about 7.0%). The enhancement was contributed to the reduction of recombination of electron–hole pairs by the application of bias potential. Decomposition of aniline by UV/bias/TiO₂ process conducted in acidic solution was enhanced noticeably with applying bias potential greater than 1.0 V because electrolysis significantly contributed to the overall decomposition efficiency of aniline.

In order to differentiate the enhancement contributed by bias potential for inhibiting the recombination of electron–hole pairs, synergistic factor was determined for quantitative calculation. Synergistic factor, *S_{pec}*, is calculated using apparent pseudo-first order rate constants listed in Table 1 for experiments using UV/TiO₂, bias/TiO₂ and UV/bias/TiO₂ processes conducted in various con-

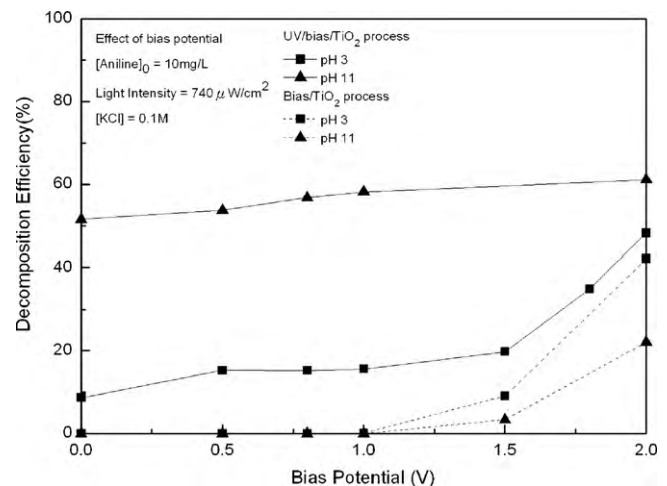


Fig. 5. Decomposition of aniline by bias/TiO₂ and UV/bias/TiO₂ processes with various applying bias potentials.

Table 1Synergetic factors determined by apparent rate constants of UV/TiO₂, bias/TiO₂ and UV/bias/TiO₂ processes.

Bias potential (V)	pH 3.0			pH 11.0		
	$k_{pec} \times 10^3$ (min ⁻¹)	$k_{ele} \times 10^3$ (min ⁻¹)	S_{pec} (%)	$k_{pec} \times 10^3$ (min ⁻¹)	$k_{ele} \times 10^3$ (min ⁻¹)	S_{pec} (%)
0	0.50 (k_{pc})	0	0	4.02 (k_{pc})	0	0
0.5	0.96	0	48.44	4.27	0	5.79
0.8	0.84	0	41.35	4.65	0	13.51
1	1.02	0	51.52	4.84	0	16.88
2	3.75	2.93	8.79	5.51	1.40	1.72

ditions:

$$S_{pec} = \frac{k_{pec} - (k_{pc} + k_{ele})}{k_{pec}} \quad (3)$$

where k_{pc} , k_{ele} and k_{pec} are the apparent rate constants of aniline decomposition using UV/TiO₂, bias/TiO₂ and UV/bias/TiO₂ processes, respectively. The difference between k_{pec} and $k_{pc} + k_{ele}$ in the numerator represented the enhancement contributed by bias potential for inhibiting the recombination of electron-hole pairs. The synergetic factor was around 50% for experiments conducted with application of 1.0 V bias potential on UV/bias/TiO₂ process in acidic solutions of pH 3, indicating that the apparent rate constant for UV/bias/TiO₂ process with 1.0 V bias potential was 50% higher than that for UV/TiO₂ process. However, the synergetic factor was merely around 17% in the alkaline solution of pH 11 because the decomposition rate constants of aniline (k_{pec}) by UV/bias/TiO₂ process in alkaline solutions were much higher than those in acidic solutions. Therefore, the enhancement of aniline decomposition by bias potential for experiments conducted in alkaline solutions was found to be much less significant than those in acidic solutions. The synergetic factors were less for experiments conducted with 2.0 V bias potential than those conducted with lower bias potentials because electrolysis became more dominant for the decomposition of aniline.

As illustrated in Fig. 6, decomposition of aniline by UV/TiO₂ process was almost unchanged for experiments conducted in acidic solutions containing various KCl concentrations. For experiments conducted in alkaline solution of pH 11, the decomposition of aniline by UV/TiO₂ process was decreased with increasing of KCl concentration. The additions of excessive chloride ions inhibited aniline decomposition due to the competitive adsorption of chloride ions on the active sites of TiO₂. These results are similar to those in the previous studies [9]. Experimental results of the aniline decomposition by bias/TiO₂ process with the presence of KCl

concentrations from 0 to 0.5 M were illustrated in Fig. 7. The decomposition of aniline by bias/TiO₂ process was not obvious with the application of 1.0 V bias potential regardless of the presence of KCl. However, the decomposition of aniline with 2.0 V applied bias potential was enhanced with increased KCl concentration present in aqueous solution. Current density of bias/TiO₂ process was measured during reaction by a potentiostat, indicating that the current intensity was increased with increasing KCl concentration as illustrated in Fig. 8. Both decomposition efficiency and current density were increased markedly with increasing KCl concentration for experiments conducted in alkaline or acidic solutions.

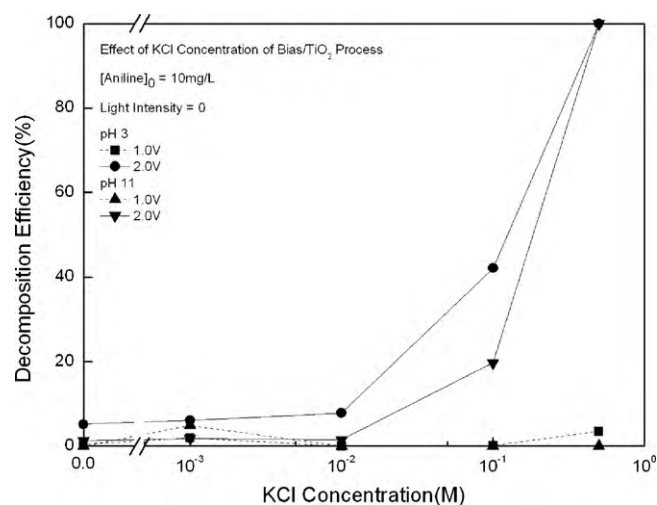


Fig. 7. Decomposition of aniline by bias/TiO₂ process in aqueous solutions containing various KCl concentrations.

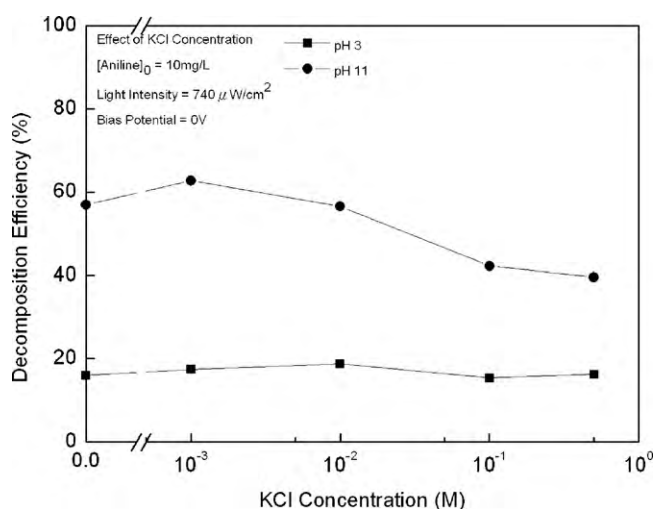


Fig. 6. Decomposition of aniline by UV/TiO₂ process in aqueous solutions containing various KCl concentrations.

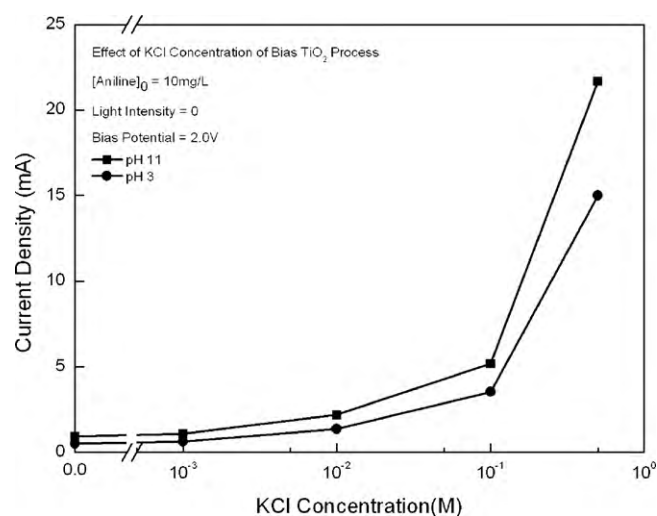


Fig. 8. Current densities measured during bias/TiO₂ process applied with 2.0 V bias potential in the aqueous solution containing various KCl concentrations.

Table 2
Energy consumption determined for aniline decomposition in alkaline solutions with various UV light intensities and bias potentials.

UV light intensity ($\mu\text{W}/\text{cm}^2$)	Bias potential (V)	Aniline decomposition (mg/L)	Energy consumption (kWh)
740	0	5.2	5.2×10^{-2} *
	0.5	5.4	
	0.8	5.7	
	1.0	5.8	
900	0	5.7	6.2×10^{-2}

* The energy consumptions by the application of bias potential were too low to be included.

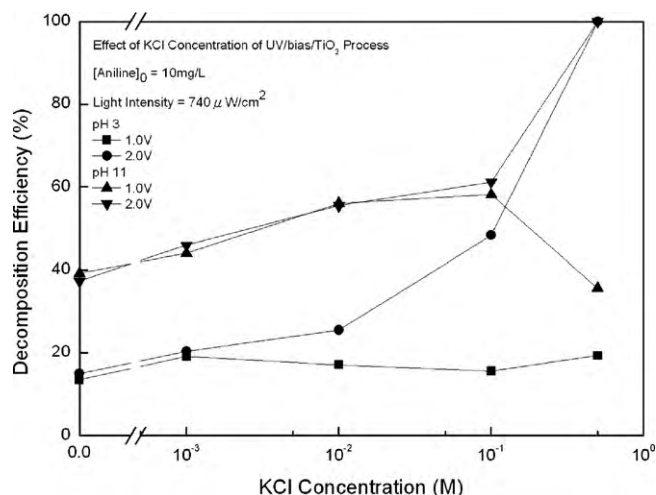


Fig. 9. Decomposition of aniline by UV/bias/TiO₂ process in aqueous solutions containing various KCl concentrations.

Effect of KCl concentration on the decomposition of aniline by UV/bias/TiO₂ process in aqueous solutions of pH 3 and 11 are shown in Fig. 9. From the results of Figs. 7 and 9, the decomposition of aniline by UV/bias/TiO₂ process was higher than bias/TiO₂ process with each KCl concentration. With the application of 2.0 V bias potential for both alkaline and acidic solutions, decomposition of aniline by UV/bias/TiO₂ process in aqueous solutions was increased with increasing KCl concentration because of the occurrence of electrolysis of aniline. By applying 1.0 V bias potential on UV/bias/TiO₂ process in alkaline solutions, the decomposition of aniline increased with increasing KCl concentration present in aqueous solution because the adsorbed chloride ions might be oxidized to free chlorine by bias potential to assist the decomposition of aniline; similar result was published by Zaroni et al. [10] for the degradation of remazol. However, the decomposition of aniline with the application of 1.0 V bias potential was noticeably reduced in aqueous solution containing 0.5 M KCl because the excessive amount of chloride ions present in aqueous solution might compete with aniline and hydroxide ions for the active sites on TiO₂ and the application of 1.0 V bias potential was not sufficient to oxidize chloride ions to free chlorines. For experiments conducted in acidic solutions applying 1.0 V bias potential, the decomposition efficiency of aniline was not varied as discussed previously for UV/TiO₂ process.

Energy consumption determined for aniline decomposition in alkaline solutions with various UV light intensities and bias potentials is shown in Table 2. The experiments were conducted under 10 mg/L of aniline concentration in a 1 L batch reactor in the aqueous solution of pH 11 for 3 h reaction. This result indicated that application of bias potential was more efficient than increasing light intensity for enhancing decomposition of aniline in this study. For instance, a 5.7 mg/L decomposition of aniline using 900 $\mu\text{W}/\text{cm}^2$ of UV light irradiation consumed 6.2×10^{-2} kWh.

However, using 740 $\mu\text{W}/\text{cm}^2$ of UV light irradiation with 0.8 V applied bias potential also exhibited similar decomposition of aniline, but only 5.2×10^{-2} kWh was consumed.

4. Conclusion

Decomposition of aniline by UV/TiO₂ process was found to be enhanced with the application of bias potential less than 1.0 V because the applied bias potential may inhibit the recombination of light-induced electron-hole pairs. However, the electrolysis of aniline in aqueous solution became more dominant as the applying bias potential exceeding 1.0 V. Experimental results indicated that the application of bias potential improved aniline decomposition more significantly in acidic solutions than that in alkaline solutions. Decomposition of aniline by UV/bias/TiO₂ process in alkaline solution increased with the concentration of potassium chloride present in aqueous solution because the adsorbed chloride ions might be oxidized to free chlorine by bias potential to assist the decomposition of aniline. However, the presence of excessive amount of KCl decreased the aniline decomposition efficiency only when it was applied a bias potential of 1 V at pH 11 because of the competitive adsorption chloride ions on the active sites of TiO₂. Experimental results also indicated that the application of bias potential consumed about 20% less energy than applying photocatalysis to achieve similar aniline decomposition.

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