

PHOTOCATALYTIC DECOLOURATION OF REACTIVE ORANGE 16 (R3R) DYE

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ABSTRACT

Photocatalytic decolouration of dyes is a new concern among researchers since it offers an attractive method for decolouration of dyes and breaks them into simple mineral forms. Commonly the method utilises a TiO₂ semiconductor and UV light. Later on to increase efficiency, the method was developed using applied potential as known photoelectrocatalysis. Experiments were carried out in a larger-scale photoelectrocatalytic reactor equipped with TiO₂ photo-anode and Ni counter electrode to degrade an azo Reactive Orange 16 (RO 16) dye. Effect of applied potential, UV irradiation, anion of electrolytes (Na₂SO₄ and NaCl) and pH has been investigated. It was found that decolouration going to faster in the present of ion chloride. To compare photoelectrocatalytic and photocatalytic method, it has been tried to use a non-woven paper (supplied by Ahlstrom) and the TiO₂ (Millenium PC500) in slurry by removing the electrodes. The rate of decolouration by photoelectrocatalytic method was very similar to that which by non-woven paper and TiO₂ in slurry.

Keyword : photocatalysis, photoelectrocatalysis, decolouration, reactive azo dye

INTRODUCTION

A lot of industries especially textile dyeing and printing industries, many of them in the developing countries such as Indonesia, have generated environmental problems like aesthetic pollution, eutrophication and perturbation of aquatic ecosystems. It was estimated that 15% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents (Zollinger, 1991). On the other report, around 200 l of water are required per kilogram of finished cotton fabric. Since the reaction to fix

these dyes to the fibers are not very efficient, therefore, residual dyes are dumped into the water and are discharged in the wastewater system (Weber and Adams, 1995).

Recently discoloration in wastewater is a current of discussion all over the world. The textile azo dyes with synthetic intermediates as contaminant and its degradation product have undoubtedly attracted the most attention with regard to high environmental impact because of their widespread use, their colour, and some azo dyes potentially to form toxic aromatic

products which have carcinogenicity and mutagenicity properties (Cisneros, Espinoza and Litter, 2002; Bilgi and Demir, 2005), beside in fact that removing this pollutant in primary and secondary treatment is quite low (Carneiro, 2004).

There are various chemical and physical processes for treating these dyes. The common physical methods, such as direct precipitation and separation or elimination by adsorption, flocculation, membrane separation, coagulation and chlorination (Zollinger, 1991), have been largely incomplete and ineffective because the problem is not completely resolved, being required further treatment. Biological processes also are limited due to the fact that many of the dyes are xenobiotic and non-biodegradable (Carneiro, 2004). Augugliaro and Hu reported that anaerobic azo dye reduction proceeded relatively slowly. Alternative methods based on advanced oxidation processes (Majcen-LeMarechal, Slokan and Taufer, 1997; Galindo and Kalt, 1999; Kuo, 1992; Zhang, 1998) combining UV irradiation and oxidative agents, but the presence of intermediates could be more harmful than the pollutant itself (Carneiro, 2004).

An attractive way to converse the textile organic compounds to their complete degradation is heterogeneous photocatalytic oxidation process. Several photocatalysts like TiO_2 , WO_3 , SnO_2 , ZnO , CdS , act via hydroxyl radical generation as powerful oxidant. Commonly, the TiO_2 semiconductor under UV irradiation has been largely used because of its photostability, non-toxicity, low cost and water insolubility under most environmental condition (Kuo, 1992; Zhang, 1998; Hachem, 2001; Epling and Lin, 2002; Silva and Faria, 2002).

Photocatalysis / Photoelectrocatalysis by Using TiO_2

A well-known process, photocatalysis using TiO_2 (generally in the anatase form), is generation of electron/hole pairs during UV irradiation of the semiconductor surface. Adsorbed water/ OH^- groups are available as electron donors to yield hydroxyl radical (OH^\bullet) while oxygen can act as electron acceptor to form the superoxide radical ion ($\text{O}_2^{\bullet-}$). Both species are strongly oxidizing to degrade organic compound like dyes [12, 13]. Nevertheless, the high rate of electron/hole pair recombination reduces the quantum yield of the TiO_2 process and represents its major drawback for photocatalytic process

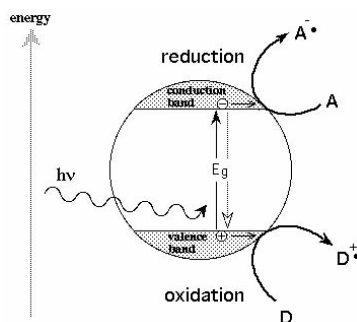
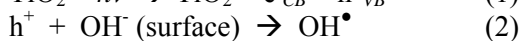
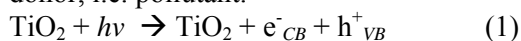


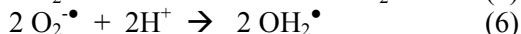
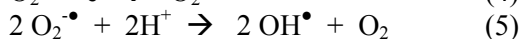
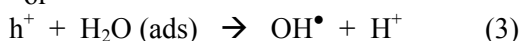
Figure 1. Photocatalysis

As shown on Fig. 1, photocatalyst absorbs photons whose energy is more than the semiconductor's band gap (3.2 eV), and the electron in valence band can transit to the conduction band. As a result, photogenerated electrons and holes are formed in the conduction band and the valence band of the semiconductor. Photogenerated electrons can make their way to the surface and reduce absorbed oxygen, ultimately to water, and photogenerated holes may oxidize any adsorbed pollutant, ultimately to its mineral forms, CO_2 and H_2O (Mills and Lee, 2004), as shown on

equation (1) to (6). In this application, A is the electron acceptor, i.e. invariably dissolved oxygen, and D is the electron donor, i.e. pollutant.



or



However, during photocatalysis most electrons and holes recombine before they reach the surface and consequently much of the absorbed energy does not generate hydroxyl radicals and simply turned into heat (Egerton and Christensen, 2004).



Photoelectrocatalysis offers an attractive method to improve the photocatalytic efficiency consists by applying a biasing potential to the photoanode and exploit the electric field enhancement effect (EFE) (Egerton and Christensen, 2004). This configuration allows the more effective separation of photogenerated charges and will increase the lifetime of electron-hole pairs.

When the TiO_2 semiconductor is irradiated with UV light with $E_{\text{light}} > E_g$, and the electrical circuit is completed by connection to an inert counter electrode, see Fig. 2., an electric field is generated in the semiconductor to a depth W (depletion layer). This internal electric field is highly dependent on the degree of doping and arises from the presence of immobilised negative charge on the semiconductor surface as well as from the bias potential. The electric field facilitates the charge separation. Any electrons/holes generated in the depletion layer W will be efficiently

transported to the bulk or surface. Absorption of radiation to the depth more than $(W + L_p)$ will results in charge recombination (the holes cannot diffuse to the surface). For any electrons/holes generated at the depth of between W and $(W + L_p)$, the photogenerated holes may diffuse to the depletion boundary layer, and the uphill to the surface of the semiconductor, where they oxidised adsorbed OH^- or water molecules to produce hydroxyl radicals. The photo-generated electrons in the conduction band may diffuse downhill into the bulk and then migrate through the external circuit into a suitable counter electrode allowing the counter electrode reaction, reduction of oxygen, and so prevent the build of negative charge at the semiconductor surface Gerischer, 1993). As a result, the possibility of recombination is minimised, and hence, the quantum efficiency improves.

The magnitude of the internal electric field, even at bias of $\sim 1\text{V}$ is sufficient to separate photogenerated electrons and holes efficiency (Butterfield, 1997).

Reactive Orange 16 Dye

Azo dyes have been largely used in a variety of products such as textile, foodstuffs and leather (Muruganandhom and Swaminathan, 2004). Azo dyes have aromatic moieties which link together by azo ($-\text{N}=\text{N}-$) chromophores.

Reactive Orange 16 (C.I. 17757) (R3R) is a reactive dye bearing an azo group as chromophore and a sulphatoethylsulfone as the reactive group. This dye was highly recommended for printing process and usually used for colouring silk and cotton (Carneiro, 2004). The molecular structure of the dye is shown on Fig 2 below :

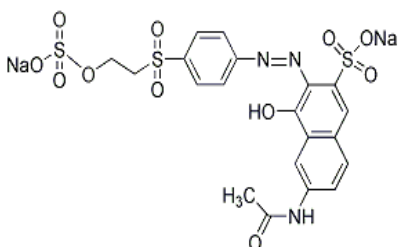


Figure 2. Molecular structure of R3R

METHODOLOGY

Photoelectrocatalytic experiments were carried on a larger-scale photoreactor equipped with UV light (2x 8W Sylvania Blacklight 350) in the volume of 600 ml in definite concentration dye solution, as shown on Fig 3.

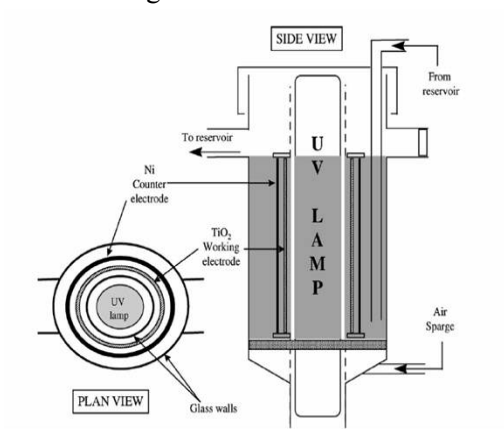


Figure 3. Photoreactor

The reactor consists of: a double-wall cylinder sealed at the bottom and electrode cassettes; a titanium dioxide photoanode processed by sol-gel method; a nickel mesh counter electrode; an axially-positioned UV lamp which was located within the inner annulus along the axis of reactor.

Reactor was connected to the electrochemical control of electrode bias which was indicated by the voltage difference applied between the electrodes shown by potentiostat and amperemeter to measure

the electric flow within the reactor. Voltage difference between two electrodes was changeable at 0, 0.6 and 1.2 volt. Reactor also was supplied by oxygen cylinder at the pressure 0.25 bar through a sparger.

The R3R dye concentration was 0.1 mM. Electrolyte solution (Na₂SO₄ or NaCl) in the concentration of 0.1 M was used. The pH was adjusted using NaOH or HCl and measured by Griffin digital pH meter. Samples were taken from photoreactor every 15 minutes until two hours. For slurry samples in the concentration of 2 g/dm³, they need to be separated from the photocatalyst before taking spectrum by centrifuging at 3000 rpm for 10 minutes using laboratory centrifuge Wifug Labor-50M.

Visible and ultraviolet spectra of each sample were recorded between 200 and 700 nm, employing a UV/Vis spectrometer (Shimadzu, model UV-1240) equipped with 10 mm silica cells and connected to the computer using UV-Probe. The degradation of RO 16 solution was followed by determining absorbance changes at 254, 297, 386, and 493 nm by using UV/Vis spectrometer.

In order to compare PC and PEC processes, by removing electrodes, non-woven paper (Ahlstrom photocatalytic media) has been tried and then compared with the heterogeneous photocatalysis in slurry using Millenium PC500 TiO₂ (100% anatase, specific surface area of 320m²/g). The non-woven material (75 g/m²) is cut and shaped around to the inside of the cylindrical anode of the photoelectrocatalytic reactor to find out the same UV flux as the TiO₂ photoanode used in the photoelectrocatalytic experiments. Guillard et al used the media, PC500 TiO₂ fixed on paper by using a binder, for degrading

amount of dyes and found out the efficiency was slightly less important than that of the powder.

RESULT AND DISCUSSION

Photodegradation of Dyes

The absorption spectral changes during photocatalytic oxidation of RO 16 are shown in Fig. 4. It is observed that the absorption spectrum of RO 16 at pH = 7 using a silica cell 10 mm is characterised by two bands in the UV region located at 254 and 297 nm, and two bands in the visible region located at 386 and 493 nm. The different observation of the band, not include the lowest wavelength of the band, has been found if the 1 mm quartz cell used. This situation is caused to the path length of the cell that affected the intensities of the incident and transmitted light as shown in Lambert-Beer's law.

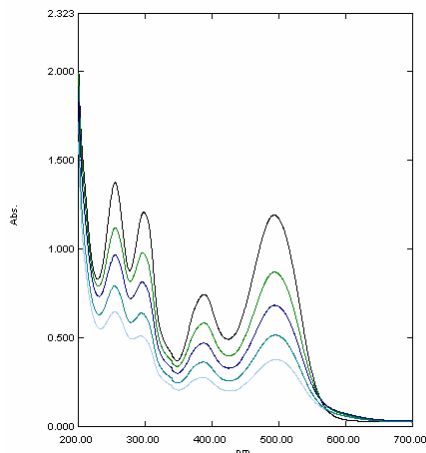


Figure 4. Spectral analysis of R3R

Fig. 4. shows that degradation of the dye at 493 nm band occurs relatively faster than 386 nm band and others. It has been concluded that firstly the initial cleavage of the chromophoric azo was followed by degradation of aromatic part, benzene and naphthalene rings, of the dye molecule.

The photooxidation reaction is pseudo-first-order with respect to azo dye concentration. The kinetic constant can be linked to the dye concentration by:

$$\ln (C/C_0) = -kt \quad (10)$$

where C is the concentration of dye at time t, C_0 is the initial concentration of dye, and k is the rate constant. The kinetic constants of Reactive Orange 16 at these wavelengths are given in Table 1. There is a correlation between UV/Vis spectral changes, from Fig. 4, and kinetic results as function of irradiation time.

Table 1. Kinetic constants of R3R

Wavelength (nm)	k x 1000 (min^{-1})
254	2.7
297	3.8
386	4.6
493	5.9

Effect of Applied Potential and UV Light

UV irradiation has a great influence to increase the photocatalytic degradation of dyes. According to the band theory, electrons are ejected from the valence band to the conduction band leaving positive holes behind when radiated with UV light energy greater than band gap. Then subsequent photodegradation reactions take place.

Fig. 5. shows the influence of applied potential and UV irradiation to the degradation of Reactive Orange at 493 nm. In the absence of UV irradiation, electrochemical degradation is not occurred. But, with UV the photocatalysis will take place rapidly even though without applied potential.

Applying a small positive potential to the TiO_2 electrode forces the photo-generated electrons to move towards the

bulk of the material and then through an external circuit to the counter electrode. The positive holes are forced to move in the opposite direction to the electrons. In this situation electrons and holes perform their reaction more efficiently, see the applied potential of 0.6V and 1.2V on the graph.

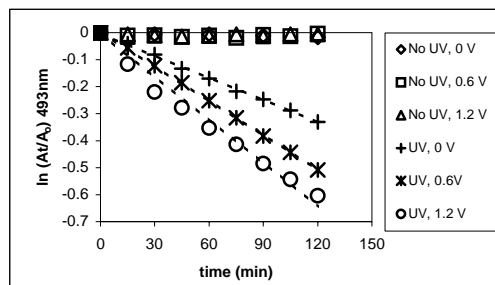


Figure 5. Effect of applied potential and UV

Effect of Anion

Some anions have substantial effect on the photocatalytic oxidation of organic pollutants. Anions affect the adsorption of the degrading species and act as hydroxyl free radical scavengers. There are two electrolytes used for experiments, i.e. sodium sulphate and sodium chloride. Fig. 6 shows that sodium chloride gives the rate of degradation higher than sodium sulphate.

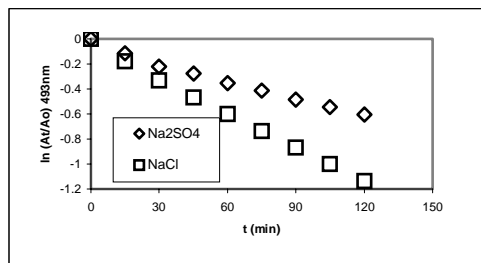


Fig. 6. Effect of Anion

Carneiro et al who used a two compartment reactor, reported that increasing rate of PEC colour removal of Reactive Orange in NaCl medium is

attributed to the chlorine formation. The content of active chlorine was determined by the DPD (N,N-diethyl-p-phenylene-diamine) colorimetric method. Chloride ion is responsible for formation of Cl^{\bullet} , Cl_2^{\bullet} , or active chlorine (Cl_2 , $HClO$, ClO^{\bullet}) as powerful oxidizing species, particularly in acidic medium. While active chlorine is detected, it seems that radical chlorine species are acting preferentially in the dye degradation.

Effect of pH

The pH has a varied effect on the photocatalytic process and it is expected that the suitable pH should affect the rate of degradation as adsorption varies with pH. In general, adsorption is maximum near the point of zero charge (pzc), at which point the photocatalytic degradation rate is also maximum (Bhatkhande, Pangarker and Beenackers, 2002).

In acidic solution, the pH is lower than pzc and hence the TiO_2 surface is positively charged. Reversely, in basic solution the surface is negatively charged.

$pH < pzc:$



$pH > pzc:$



Since Reactive Orange 16 is negatively charge, it is conceivable that at acidic medium the electrostatic attraction between positively charged TiO_2 surface and negatively charged sulfonic group leads to strong adsorption. And at basic medium, TiO_2 surface becomes negative and so it is electrostatically repulsive to the negative charged dye molecule. However, lowering of the pH creates the TiO_2 particles to aggregate and consequently reduces the adsorption of the dye on to the TiO_2 surface (Muruganadham and Swaminathan, 2006).

Fig. 7. below shows that in the present of sodium sulphate as electrolyte, Reactive Orange degradation reach a maximum rate on pH = 7, but at both pH = 4 and pH = 10 are lower.

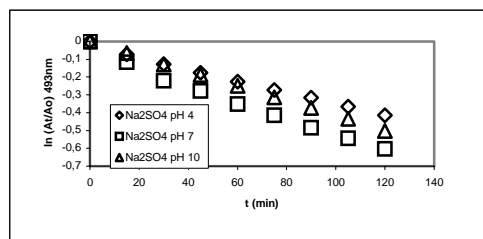


Figure 7. Effect of pH

An alternative approach of TiO₂ immobilised on a non-woven paper (supplied by Ahlstrom). The rate of degradation using non-woven paper is faster in NaCl than in Na₂SO₄ and reaches the highest rate at pH = 7, as seen on Table 2.

Table 2. Rate constants of RO 16 photodegradation using non-woven paper

pH	k x 1000 (min ⁻¹)	
	Na ₂ SO ₄	NaCl
pH 4	4.2	7.5
pH 7	6.7	8.3
pH 10	6.1	6.1

At pH = 7 and in Na₂SO₄ electrolyte, the rate of decolouration for PEC (sol gel electrode) and PC using both TiO₂ of PC500 in slurry and the non-woven paper is very similar, see Fig. 8. In NaCl electrolyte at the same pH, rate of decolouration of RO 16 in PEC and non-woven paper is very closed, as shown on Fig. 9. However, the activity of the paper decreased significantly if it was washed between runs, Fig. 10. It was caused by amount of TiO₂ particles liberated to the solution.

The disadvantage of PC in slurry is that the TiO₂ particles have to be separated from treated effluent. Ahlstrom has developed a photocatalytic slurry/coating process to coat substrate to avoid the necessary postfiltration stage. It uses an inorganic binder that can transmit UV radiation but not destroyed by photocatalysis.

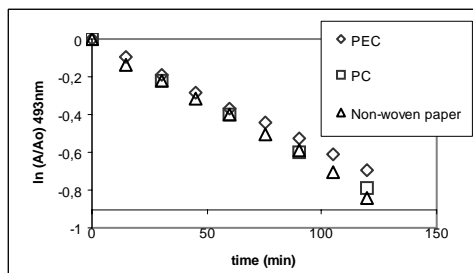


Figure 8. Comparison of PC slurry, PEC and PC with paper in Na₂SO₄

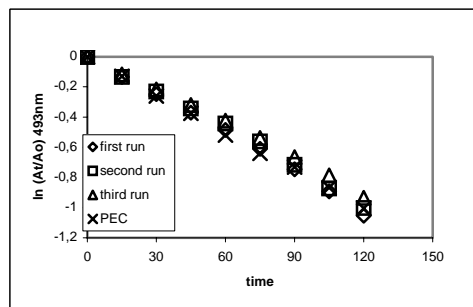


Figure 9. Comparison of PEC and repetitive unwash run of paper in NaCl

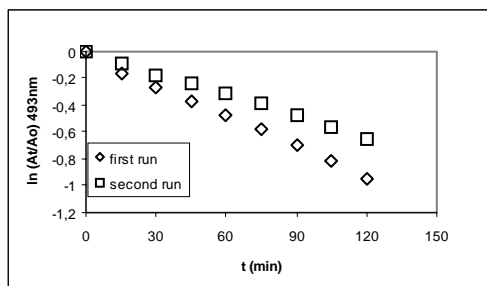


Figure 10. Effect of washing on paper

CONCLUSIONS

- 1) Photocatalysis (PC) and photoelectrocatalysis (PEC) are alternative methods for decolourating textile wastes.
- 2) PEC is still less effective than PC, and this is attributed to reduced mass transfer and/or limited UV penetration.
- 3) The PEC and PC rates for the bleaching of R3R were similar for the two immobilized systems.
- 4) Photocatalysis in slurry is the most efficient, in NaCl electrolyte RO 16 degradation is ~82% at pH 4 and, in Na₂SO₄ electrolyte is ~61% at pH 10.

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