

**REMOVAL OF METHYL ORANGE USING PHOTOACTIVATED
TITANIUM DIOXIDE IMMOBILIZED ON GRANULAR
ACTIVATED CARBON**

LAM SZE MUN

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TUDUL: REMOVAL OF METHYL ORANGE USING TITANIUM DIOXIDE
(IMMOBILIZED ON ACTIVATED CARBON)

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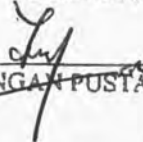
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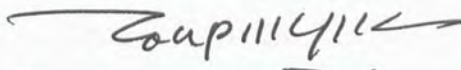
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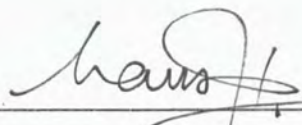
Name: Lam Sze Mun

Title: Photocatalytic Removal of Methyl Orange using TiO_2 immobilized on Granular Activated Carbon



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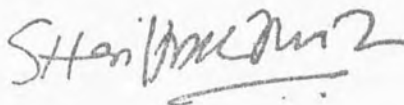
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ASSOC PROF DR. MARCUS JOPONY



DR. MD. LUTFOR RAHMAN



DEAN

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ABSTRACT

Removal of Methyl orange (MeO) in aqueous solution using photoactivated TiO_2 immobilized on granular activated carbon (TiO_2/GAC) in the present of UV-A radiation was studied. The TiO_2/GAC was prepared through precipitation of titanium hydroxide from titanium tetraisopropoxide and followed by heat treatment. The removal of MeO was carried out in a 500-mL cylindrical photo-reactor. The results indicate that the TiO_2/GAC has higher reactivity for the removal of MeO in aqueous solution under compared to $\text{TiO}_2(\text{pyrex})$ and GAC systems. The best experimental condition was obtained by 2-layered $\text{TiO}_2/\text{GAC}/\text{UV-A}$ system, where 74% of the MeO in aqueous solution ($[\text{MeO}] = 1 \times 10^{-4} \text{ mol L}^{-1}$) was successfully removed. Study on the kinetic of removal of MeO solution in the $\text{TiO}_2(\text{pyrex})/\text{UV-A}$, $\text{GAC}/\text{UV-A}$ and $\text{TiO}_2/\text{GAC}/\text{UV-A}$ systems shows that the systems was conform to pseudo-first order reaction with the rate constant, k of the best system is equal to 0.0107 min^{-1} .

*PENYINGKIRAN METIL OREN MENGGUNAKAN FOTOAKTIVASI
TITANIUM DIOXIDE IMMOBILISASI PADA BUTIRAN
KARBON TERAKTIF*

ABSTRAK

Penyingkiran Metil Oren (MeO) dalam larutan akueus menggunakan fotoaktivasi TiO₂ immobilisasi pada butiran karbon teraktif (TiO₂/GAC) dengan kehadiran sinaran UV-A telah dikaji. TiO₂/GAC telah dihasilkan melalui pemendakan titanium hidroksida daripada titanium tetraisopropoksida dan diikuti dengan rawatan pemanasan. Pemangkinanfoto penyingkiran MeO telah dijalankan dengan menggunakan fotoreaktor 500-mL. Keputusan eksperimen menunjukkan bahawa TiO₂/GAC telah meningkatkan fotoaktiviti dalam larutan akueus MeO berbanding dengan system TiO₂(pyrex) dan GAC. Keadaan eksperimen yang terbaik didapati ialah sistem 2-lapis TiO₂/GAC/UV-A, dimana 74% larutan akueus MeO ($[MeO] = 1 \times 10^{-4} \text{ mol L}^{-1}$) telah disingkirkan. Kajian terhadap kinetik penyingkiran MeO dalam sistem TiO₂(pyrex)/UV-A, GAC/UV-A dan TiO₂/GAC/UV-A menunjukkan bahawa sistem tersebut telah mematuhi tertib pertama-pseudo dengan pemalar kadar, k pada sistem yang terbaik adalah 0.0107 min^{-1} .



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LIST OF SYMBOLS & ABBREVIATIONS

TiO_2/GAC	Titanium dioxide immobilized on granular activated carbon
GAC/UV-A	Granular Activated Carbon-suspension photocatalytic system
$\text{TiO}_2(\text{pyrex})/\text{UV-A}$	Titanium dioxide photocatalytic system
$\text{TiO}_2/\text{GAC}/\text{UV-A}$	Titanium dioxide immobilized on granular activated carbon photocatalytic system
UV-A	Wavelength of Ultra Violet-Visible light range in 320-400 nm
UV-vis	Ultra Violet-Visible light
AOP	Advance oxidation process
Abs	UV-visible absorbance
$\%D_{\text{Abs}}$	Degradation degree
A_t	Absorptivity at contact time, t
A_0	Initial absorptivity
k	Pseudo-first order rate constant
e^-	Electron
h^+	Hole
$h\nu$	Photon energy



CHAPTER 1

INTRODUCTION

1.1 DYESTUFFS AND ADVANCE OXIDATION PROCESSES IN WASTEWATER TREATMENT

Dyestuffs and other commercial colourants have become the focus of environmental remediation efforts because of their natural biodegradability is made increasingly difficult owing to improve properties of dyestuffs. Considering both the volumes and the chemical composition of the discharged effluent, textile dyeing and finishing industries are one of the major pollutants among industries sectors (Robert and Malato, 2002; Bizani *et al.*, 2006). The effluent is well known to contain strong colour, high chemical oxygen demand (COD) contents and low biodegradability. Furthermore, recent studies indicated that approximately 15% of synthetic dye is lost annually during manufacturing and processing operations and 20% of the resultant colour enters the environment through effluents from industrial wastewater treatment plants (Sauer, *et al.*, 2002; Habibi *et al.*, 2005).

Dyes have been identified as the most problematic compounds due to their strong colour property and highly molecular structure constitution. The dye molecules are insufficient removed by ordinary activated sludge systems or any biological,

chemical and physical methods in which these methods only transfer dyes molecule to another phase (Wang *et al.*, 2005; Zhang *et al.*, 2006). Among chemically synthesized dyestuffs, azo dyes that are less sensitive to temperature, liquor ratio, salinity and variable pH of solution are produced in the largest quantities. It was reported that 700,000 tons of dyes are produced in the world and about 50% among them are azo compounds that have the chromophore of N=N unit in their molecular structure (Habibi *et al.*, 2005). These azo dyes are known to be highly resistant in aerobic conditions and under anaerobic conditions they can be reduced to potentially carcinogenic intermediates (Tanaka, *et al.*, 2000).

Many researchers have reported that azo dyes can be decolourized by advanced oxidation processes (AOPs). AOPs are ambient temperature process involving the formation of hydroxyl radical (HO•) that aggressively and almost indiscriminately oxidize and mineralize the organic pollutants to water and carbon dioxide (Chen *et al.*, 2004; Liu *et al.*, 2005). Among the AOPs, titanium dioxide (TiO₂) mediated heterogenous photocatalytic treatment are capable of absorbing near UV spectral region (300 nm <wavelength< 400 nm) to initiate radical reactions. However, TiO₂ (photocatalysts) are often applied as suspensions and yet problems such as catalysts leaching, settling, floatation and the need for eventual catalyst separation by filtration during post treatment and eventually hinder their wide scale application in industry (Yu *et al.*, 2005).

On the other hand, since the concentrations of the pollutants to be decomposed are at parts per million levels or less in most cases as a result they are low frequent collision with TiO₂ makes the reaction rate of mineralization very low. Hence, it is



required to a special technique that enables the TiO_2 to decompose pollutants with high reaction rates and may be easily applied to industry (Sakthivel *et al.*, 2003). Therefore, many researchers were focused on the preparation as well as on the modification of TiO_2 and several simple coating of catalyst over glasses, ceramics and polymers were also proposed (Li *et al.*, 2006).

Many researchers have reported that the combined roles of granular activated carbon (GAC) and TiO_2 showed a synergic effect on the efficient removal of some organic compounds in the photocatalytic process (Matosa *et al.*, 2002; Tryba *et al.*, 2003). The GAC is widely used as co-adsorbent to remove organic substances of dilute concentration from water and air atmosphere. Therefore, when the TiO_2 is coated on these GAC, the organic substances are selectively adsorbed on adsorbent supports and resulted in higher concentration environments around the coated TiO_2 . Subsequently, the adsorbed substances are then transferred into the TiO_2 by adsorption and decomposed in high photodestruction reaction rate under UV-A irradiation (Tariq *et al.*, 2005). Such a system would be particularly effective for the removal of large volumes of polluted waters and totally mineralized or oxidized at their higher degree respectively into less harmful compounds (Li *et al.*, 2006).

1.2 OBJECTIVE

Strong colourant in the dye-containing wastewater is the most typical characteristic of the dyestuffs because it brings negative impact to the aquatic ecosystem and its derivatives are highly dangerous for human being. Therefore, this research is focused on the photocatalytic removal of simulated wastewater, Methyl Orange (MeO) solution using semiconductor TiO_2 immobilized on granular activated carbon (GAC) as the treatment method. The objectives of this research are:

- (i) to prepare TiO_2 immobilized on GAC,
- (ii) to determine the effect of different TiO_2 layers coated on GAC towards the removal of MeO in aqueous solution.

1.3 SCOPE

Photocatalytic removal of aqueous azo dye, Methyl Orange (MeO) in aqueous solution by TiO_2 immobilized on GAC had been investigated. The primary stage of this research was to prepare TiO_2 sol-gel, TiO_2 sol gel coat with GAC granular and MeO stock solution. The study was conduct in lab-scale using a cylindrical photo-reactor (500-mL capacity) with MeO in aqueous solution. Subsequently, the performance of TiO_2 /GAC/UV-A system had been examined toward the removal of MeO with different layers of TiO_2 immobilized on GAC.

CHAPTER 2

LITERATURE REVIEW

2.1 DYE-CONTAINING WASTEWATER

Dyes are organic compounds characterized by the presence of unsaturated groups (chromophores) in the molecular structure, which consist of double and triple bonds such as $-C=C-$, $-N=N-$, $-C\equiv N-$, whose function is to shift the radiation absorption in the visible range (Safarik *et al.*, 2002). Other functional groups characterizing this class of compounds are the auxochromes such as $-NH_2$, $-OH$, $-COOH$, $-SO_3H$, that responsible to increase the colour intensity.

More than 30,000 commercial dyes based on 8,000 different chemical structures are used in textile, food, pharmaceutical, paper and ink industries (Molinari *et al.*, 2004). However, the dye molecules have received the largest attention due to their strong colour property and highly molecular structure constitution, although dyes are often not the largest contributor to the wastewater. Dyes concentration in wastewaters is usually low but due to their strong colour, they are visible even at very low concentrations, thus causing serious aesthetic and pollution problems in wastewater disposal (Zollinger, 1999).

When these wastewaters are discharged into water without proper treatment, the dyes are transported over long distances because of their high solubility and some are hydrolyzed or anaerobically metabolized to form carcinogenic end products (Guillard *et al.*, 2003; Gultekin and Ince, 2006). Moreover, effluent streams coming from dyeing industrial plants are highly variable in composition with relatively high biological oxygen demand (BOD) and chemical oxygen demand (COD) contents. Therefore, the dye-containing wastewater treatments are focused not only to solve the environmental impact but also to allow water to be reused.

2.1.1 Methyl Orange

Methyl orange (MeO) is a kind of azo dyes that constitute a significant portion of dye colourants. Azo dyes are coloured organic compounds that have been used in industry for applications such as textiles, papers, leathers, gasoline, additives, foodstuffs and cosmetics and analytical chemistry (Habibi *et al.*, 2005). The azo dyes contains one or more nitrogen to nitrogen double bonds ($-N=N-$) and they can be grouped as monoazo, diazo, triazo according to the number of azo bonds in its structure (Bell and Buckley, 2004; Silva *et al.*, 2006).

MeO (Sodium *p*-Dimethylaminoazobenzenesulfonate), with the molecular formula $C_{14}H_{14}N_3O_3SNa$ and the molecular weight of $327.34 \text{ g mol}^{-1}$. MeO is also called Acid Orange 52, Dexon, Methyl Orange B and Orange 3. It has an orange appearances and in solid physical state which is chemically stable under normal temperature and pressure (Wang *et al.*, 2006).

MeO is also an acid dye or anionic dye. It is characterized by the sulphonate group ($-\text{SO}_3\text{Na}$), which are responsible for the high solubility of this dye in water (Mrowetz *et al*, 2003; Sackheim and Lehman, 1998). Therefore, the MeO dye that containing these group will readily dissociated into a coloured anion in the dye bath. The transition range of MeO can be varies from pH 3.1 to 4.4 and absorbs wavelength of light at 471 nm to 504 nm, hence the appearing colour affected by the wavelength of absorption and pH respectively. The structural formula of MeO is shown in Figure 2.1.

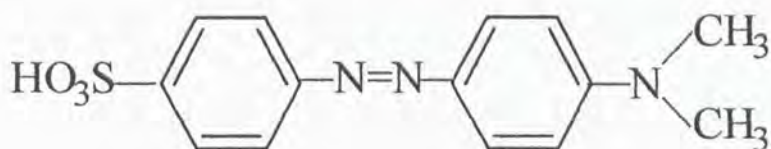


Figure 2.1 The structural formula of Methyl Orange.

The MeO is often chosen as an indicator that used in titration because of its clear colour change. As the hydrogen ion is lost or gained, there is a shift in the exact nature of the delocalization in the molecule and causing a shift in the wavelength of light absorbed, which results a different colour. MeO is red in solution of pH less than 3.1 and it is yellow at pH greater than 4.4. The characteristic clear colours of MeO solutions also make it an important dye for the textile and photographic industry (Kwon *et al.*, 2006).

2.2 CONVENTIONAL WASTEWATER TREATMENT

To date, minimizing the use of dyes in the production and preventing the disposal of spent dye bath in the wastewater, did not result in 90% of the dyes removal (Habibi *et al.*, 2005). Adequate treatment of these waters is of primary concern in order to preserve the natural ecosystem. Therefore, a variety of physical methods, such as adsorption, biological methods (biodegradation) and chemical methods (chlorination, ozonation) are the most frequently used for treatment of dye wastewater (Sonawane *et al.*, 2004).

Biological systems are most commonly used by the industry. They are economically effective in removing contaminants from wastewater but however, with the use of non-biodegradable chemicals particularly dyes in textile mills and other industries, the microorganisms that are normally being depended upon in the biological seem to be helpless. The processes by bacteria beds are less adapted because of the flocculation of the wastewater composition (Sanroman *et al.*, 2004).

The use of conventional oxidants has been for years the standard chemical method for the treatment of dye wastewaters. However, these procedures are not always feasible owing to the thermodynamic and kinetic limitations of common reagents to attack refractory compounds (Bizani *et al.*, 2006). Ozone and hypochlorite oxidants are efficient decolourization methods but they are not desirable because of the high operating cost and the secondary pollution arising from the residual chlorine (Wu, 2004).

Other methods such as flocculation, reverse osmosis and absorption on activated carbon have also been tested. The drawbacks of these methods are mainly the creation of a more concentrated pollutant-containing phase. Their success are rather limited for some dyes especially reactive dyes, due to their relatively low molecular weight, chemical stability, high solubility and low physical affinity for these absorbents (Frijtersa *et al.*, 2006). Furthermore, these processes just transfer pollutants from one phase to another rather than eliminating them from the water matrix (Sauer *et al.*, 2002).

Due to the ineffectiveness of the conventional wastewater treatment, it is necessary to find an effective method of wastewater treatment capable of removing colour and degrading toxic organic compounds from industrial effluents. As an alternative or integration to the conventional processes, advanced oxidation technologies have been proposed (Tariq *et al.*, 2005).

2.3 ADVANCE OXIDATION PROCESSES

Advanced oxidation processes (AOPs) have been utilized to oxidize complex organic constituents found in wastewater that are difficult to degrade biologically into simpler end products (Chen *et al.*, 2004; Kwon *et al.*, 2006). When conventional chemical oxidation is used, it may not be necessary to oxidize completely a given compound or group of compounds. In many cases, partial oxidation is sufficient to render specific compounds more amenable to subsequent biological treatment or to reduce their toxicity (Tchobanoglous *et al.*, 2004).



AOPs typically involve the generation and use of the hydroxyl free radical ($\text{HO}\cdot$) as a strong oxidant to destroy compounds that cannot be oxidized by conventional oxidants such as oxygen, ozone and chlorine (Tariq *et al.*, 2005; Konstantinou and Albanis *et al.*, 2004). The relatively oxidizing power of the hydroxyl radical, along with other common oxidants is summarized in Table 2.1 (Molinari *et al.*, 2004).

Table 2.1 Comparison of oxidizing potential of various oxidizing agents.

Oxidation species	Oxidation potential, eV
Fluorine	3.06
Hydroxyl radical	2.80
Nascent oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.77
Perhydroxyl radical	1.70
Hypochlorous Acid	1.49
Chlorine	1.36

(Source: Molinari *et al.*, 2004)

As shown, with the exception of fluorine, the hydroxyl radical is one of the most active oxidants known. The hydroxyl radical reacts with the dissolved constituents, initiating a series of oxidation reactions until the constituents are completely mineralized (Huang *et al.*, 2001; Pekakis *et al.*, 2006). Non-selective in their mode of attack and able to operate at normal temperature and pressure, hydroxyl radicals are capable of oxidizing almost all reduced materials present without restriction to specific classes of groups of compounds as compared to other oxidants.

Presently, a variety of technologies are available to produce $\text{HO}\cdot$ in the aqueous phase. The various technologies are summarized in Table 2.2. However, only

ozone/UV, ozone/hydrogen peroxide, ozone/UV/hydrogen peroxide and hydrogen peroxide/UV are being used on a commercial scale (Huang *et al.*, 2001).

Table 2.2 Example of technologies used to produce the reactive hydroxyl radical.

Ozone-based processes	Non-ozone-based processes
Ozone at elevated pH (8 to >10)	H ₂ O ₂ + UV
Ozone + UV ₂₅₄ (also application in the gas phase)	H ₂ O ₂ + UV + ferrous salts (Fenton's reagent)
Ozone + H ₂ O ₂	Electron-beam irradiation
Ozone + UV ₂₅₄ + H ₂ O ₂	Electronhydraulic cavitation
Ozone + TiO ₂	Ultrasonics
Ozone + TiO ₂ + H ₂ O ₂	Nonthermal plasmas
Ozone + electron-beam irradiation	Pulsed corona discharges
Ozone + ultrasonics	Photocatalysis (UV + TiO ₂)
	Gamma radiolysis
	Catalytic oxidation
	Supercritical water oxidation

(Source: Huang *et al.*, 2001)

The main advantages of these methods are high rates of pollutant oxidation, flexibility concerning water quality variations and small dimension of the equipment. On the other hand, the disadvantages are relatively high treatment costs and special safety requirements because of the use of very reactive chemicals (ozone, hydrogen peroxide) and high-energy sources (UV lamps, electron beams, radioactive sources) (Bizani *et al.*, 2006).

2.4 HETEROGENEOUS PHOTOCATALYSIS

Among the advanced oxidation processes (AOPs), heterogeneous photocatalysis appears as an emerging destructive technology leading to the total mineralization of most of the organic pollutants. The heterogeneous photocatalytic system consists of semiconductor particles (photocatalyst) which are in close contact with a liquid or

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