

Photocatalytic Degradation of Dissolved Organic Matter in the Ground Water Employing TiO₂ Film Supported on Stainless Steel Plate

Penguraian Zat Organik Terlarut dalam Air Tanah secara Fotokatalisis Menggunakan Lapisan Tipis TiO₂ pada Plat Stainless Steel

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ABSTRACT

Photocatalytic Degradation of Dissolved Organic Matter in The Ground Water Employing TiO₂ Film Supported on Stainless Steel Plate. The Taman Palem Residences, Cengkareng, Indonesia has a groundwater problem as a main sources of drinking water in the area due to yellowish brown colour of the water, that may come from dissolved organic matter (DOM), humic substances. Photocatalytic degradation using TiO₂ coated on a stainless steel plate (8 x 8 cm) to degrade the dissolved organic matter was studied. Groundwater samples were collected at 150 m deep from Taman Palem Residences. The TiO₂ catalyst was made from deep coating in a sol-gel system of titanium (IV) diisopropoxidebisacetylacetonate (TAA) precursor and immobilized at stainless steel plate (8 x 8 cm), followed by calcination at 525°C. Two catalyst sheets were put in batch reactor containing groundwater. The ground water containing DOM were irradiated by UV black light at varying initial pH values i.e 5, 7 and 9. Sampling of solution was taken at the interval time of 0, 1, 2, 4, and 6 hours. DOM residu in water before and after irradiation were measured by spectrophotometer UV-Vis at 300 nm. Photocatalytic degradation of DOM was greater in acid solution than in basic solution. The determination of intermediate degradation products by HPLC revealed that oxalic acid was detected consistently.

Keywords : Dissolved organic matter (DOM), groundwater, photocatalytic, TiO₂

ABSTRAK

Penguraian Zat Organik Terlarut dalam Air Tanah secara Fotokatalisis Menggunakan Lapisan Tipis TiO₂ pada Plat Stainless Steel. Perumahan Taman Palem, Cengkareng, Indonesia memiliki masalah air tanah sebagai sumber utama air minum di daerah tersebut karena warna air coklat kekuningan mungkin berasal dari bahan organik terlarut (DOM), zat humat. Telah dipelajari penguraian bahan organik dengan proses fotokatalitik menggunakan TiO₂ yang dilapiskan pada plat stainless steel (8 x 8 cm). Sampel air tanah di perumahan Taman Palem diambil dengan kedalaman 150 m. Katalis TiO₂ dibuat dengan melapiskan titanium (IV) diisopropoxidebisacetylacetonate dengan cara sol-gel pada plat stainless steel (8 x 8 cm), diikuti kalsinasi pada suhu 525°C. Dua lembar katalis dimasukkan ke dalam reaktor yang mengandung air tanah. Air tanah yang mengandung DOM

diiradiasi oleh lampu UV pada pH awal 5, 7 dan 9. Pengambilan sampel larutan diambil dengan interval waktu 0, 1, 2, 4, dan 6 jam. Sebelum dan sesudah iradiasi, residu DOM dalam air diukur dengan spektrofotometer UV-vis pada 300 nm. Penguraian fotokatalitik DOM lebih besar dalam larutan dalam keadaan asam dibandingkan dengan dalam keadaan basa. Penentuan hasil penguraian dengan HPLC menunjukkan adanya senyawa asam oksalat.

Kata kunci : Dissolved organic matter (DOM), air tanah, photocatalytic, TiO₂

INTRODUCTION

Water is one of the important commodities for human life, unfortunately the water that comes from surface and groundwater is highly contaminated. One case occurred in Taman Palem, Cengkareng, Indonesia, where drinking water has a problem, due to its colour. The colour of the water is yellowish brown, this may be caused by the high organic content of dissolved organic matter (DOM). DOM, according to an operational definition, is organic carbon smaller than 0.45 μm in diameter. At the molecular level, most of the DOM comes from polymeric organic acids called humic substance. These yellow organic acids (1000-2000 MW) are polyelectrolytes of carboxylic, hydroxyl, and phenolic functional groups. They compose 50-75% of the DOM. These substances are a potential pollution to in water, it is undesirable due the possibility to produce esthetically problems such as color in the water [1]. In spite of that, the humic acids have a significant role in the aquatic systems, they can react with heavy metals and organic pollutants such as pesticides, insecticides, and herbicides to produce complex substances [1].

Water treatment processes of DOM by conventional method usually used coagulation-flocculation-sedimentation-filtration and disinfection with chlorine process. Humic substances stabilize dispersed and colloidal particles during coagulation proses and colloidal particles can occur through the adsorption of the higher-molecular-weight humic substances on the surface of the mineral particles. A strong interaction is often observed between the dissolved humic substances and the

flocculants. In most cases, higher humic substances concentration means larger flocculants dosages and therefore higher treatment cost. Humic substances serve as precursors of potentially hazardous trihalomethanes and complex high-molecular-weight chlorinated compounds during chlorination processes. All of these compounds may have adverse effects on human health [1,2,3]. Therefore, alternative techniques to solve the problems are needed.

Photocatalytic oxidation of organic pollutant has been studied by a number of researchers. Titanium dioxide as photocatalyst has been proposed to solve various environmental problems. It is useful for inactivation of *E. coli* [4], and it destroys a wide variety of toxic and persistent organic compounds to harmless inorganic such as mineral acids, carbon dioxide and water [5,6,7].

In this paper, we report our study of photocatalytic degradation of dissolved organic material (humic substances) in the groundwater using TiO₂ immobilized on stainless steel and under black light irradiation in a batch system.

EXPERIMENTAL SECTION

Materials

TiO₂ catalyst was prepared by calcination of sol-gel film produced from titanium (IV) diisopropoxidebisacetylacetonate (TAA) precursor at 525 °C. The TAA was purchased from Aldrich. Other chemicals such as isopropanol, acetic acid, formic acid, phosphate acid, oxalic acid, methanol, chloride acid, NaOH, KMnO₄, H₂SO₄ were obtained from Merck. Methanol

used was HPLC grade. Sample of groundwater was taken at 150 m depth on Palem Garden, Cengkareng, Indonesia,

Photocatalytic reactor

Photocatalytic reactor was constructed from a Pyrex vessel (25 cm x 11 cm x 7 cm), and two catalyst sheets (8 cm x 8 cm) were placed in it. In the beginning of experiment the intensities were 1.9, 2.3, and 1.9 mW/cm² at the left, centre and right of reactor respectively and the last experiment the intensities were 1.6, 2.0 and 1.6 mW/cm² at the same position respectively.

Method of irradiation

Irradiation of groundwater sample containing DOM was conducted at various pH (5, 7, and 9). The pH of the DOM was adjusted by the addition of HCl or NaOH. The irradiation of solution was done for 1, 2, 4, 6 hour with batch system. During irradiation the solution of ground water was homogenized using magnetic stirrer. Two of 10 W UV black light lamps (TOKI, Japan), were positioned at 8 cm above pyrex vessel (Fig. 1). The intensity of UV light was measured by UV ray radiometer.

Chemical analysis

The pH of the solution before and after irradiation were measured by pH meter. Humic substances residue in water before and after irradiation were measured using Hewlett Packard Model 8453 Diode Array Spectrophotometer at 300 nm. Determination of DOM residues in water were done by titrimetry as KMNO₄. Degradation product of photocatalytic was performed by HPLC, Shimadzu model LC-9A equipped with UV detector at 210 nm, and C-18 phenomenex column. The mobile phase was 10% methanol in phosphate buffer (pH 3.4) with the flow rate of 1 ml/min.

Characterization of TiO₂ catalyst using x-ray diffraction

The surface of the TiO₂ was characterized using x-ray diffraction (XRD)

to find out the structure and dimension of the crystal that formed on the surface of the plate.

RESULTS AND DISCUSSION

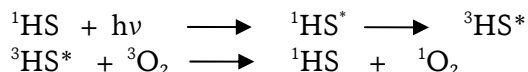
Characterization of TiO₂ crystal using XRD

The TiO₂ catalyst film that formed on the surface of stainless steel plate characterization was done using XRD. Based on X-ray data (Table 1), comparison of d value between measurement and interpretation of TiO₂ synthetic crystal with database, the crystal structure was predominantly found to be in the anatase form.

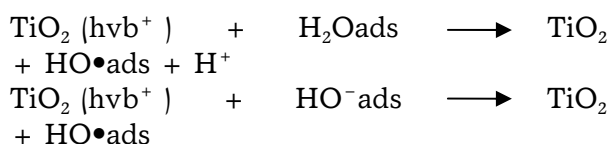
Photocatalytic and photolysis of DOM

Study on the degradation of DOM in groundwater was carried out at various treatment. The treatments were irradiation in the presence of TiO₂ (photocatalytic), irradiation in the absence of TiO₂ (photolysis) and control experiment (in the presence of TiO₂ without irradiation). Degradation of DOM during photocatalytic, photolysis, and control experiment were done at various of pH (5, 7, 9). The curve of degradation of DOM due to photocatalytic, photolysis, and control experiment were shown in Fig. 2.a, b, and c. It showed that for all pH, on control experiment, the DOM of ground water did not degrade, it may be adsorbed on surface of TiO₂. The DOM in groundwater which was irradiated by UV in the absence of TiO₂ catalyst for all pH indicated that the number of DOM degraded increase gradually as the irradiation time increased. The same profiles were observed when the DOM in groundwater was irradiated by UV in the presence of TiO₂ catalyst. The degradation of DOM molecules at the solution in the presence of TiO₂ catalyst was faster than that in the absence of TiO₂. It could be explained that DOM act as sensitizers or precursor for the production of reactive oxidants such as singlet oxygen, humic-

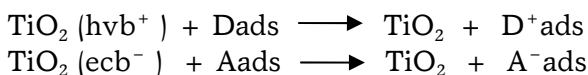
derived peroxy radicals, hydrogen peroxide, solvated electron, and $\cdot\text{OH}$ radicals [8]. Humic substances are high molecular-weight materials resulting from oxidative decomposition of plant and animal residues, singlet oxygen photoproduction in natural waters containing humic substances (HS) may be described by this reaction [8].



The reactive species formed in the solution might play as a major role in the degradation of most nonbiodegradable compound, even humic substances. For the solution irradiated by UV in the presence of TiO_2 , degradation of DOM due to combination of direct photolysis and indirect photolysis. $\cdot\text{OH}$ radicals in the solution were produced from DOM which act as sensitizers due to direct photolysis and also from TiO_2 catalyst (indirect photolysis). The mechanism of $\cdot\text{OH}$ generation in heterogeneous photocatalysis is a complex sequence of reactions. However, PIRKANNIEMI [9] suggested that the heterogeneous photocatalysis reaction follows five steps. These are: "(i) diffusion of reactants to the surface, (ii) adsorption of reactants onto the surface, (iii) reaction on the surface, (iv) desorption of products from the surface, and (v) diffusion of products from the surface. There are two routes through which OH radicals can be formed. The reaction of the valence-band "holes" ($h\nu b^+$) with either adsorbed H_2O or with the surface of OH^- groups occurs on the TiO_2 particle.

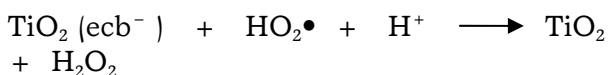
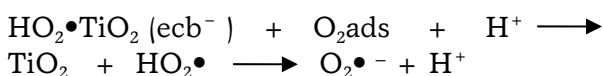


In general, donor (D) molecules such as H_2O will adsorb and react with a hole in the valence-band and an acceptor (A) such as dioxygen will also be adsorbed and react with the electron in the conduction band (ecb^-), according to reaction below.

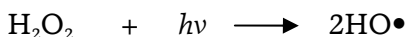


It is generally accepted that oxygen plays an important role. Oxygen can trap conduction-band electrons to form superoxide ion ($\text{O}_2\cdot^-$), These superoxide ions can react with hydrogen ions (formed by splitting water), forming :

H_2O_2 could be formed from $\text{HO}_2\cdot$ via reactions.



Cleavage of H_2O_2 by one of the reactions may yield an OH radical.



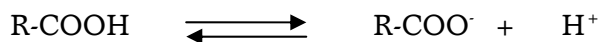
It was clear that degradation of DOM at the solution in the presence of TiO_2 catalyst was faster than that in the absence of TiO_2 .

Effect of pH on the photocatalytic degradation of DOM

Effect of pH on photocatalytic degradation of DOM is shown in Fig. 3. The change of pH during photodegradation experiment was slightly decrease to only 0.5 units from the original values. As shown in Fig. 3, the photocatalytic degradation in basic solution (pH 9) is lower than that in neutral and acidic solution. The achievement of the degree of degradation of DOM at pH 5 after irradiation for 6 hours is 63%, while at pH 7 and 9 are 47% and 13%, lower than that at pH 5, respectively.

The molecular structure of DOM depend on the pH solution. Humic acids contain both hydrophobic and hydrophilic functional groups mainly in the carboxyl, phenolic hydroxyl, alcoholic hydroxyl and carbonyl forms [8]. At higher pH, more functional groups were ionized to yield a

larger negative charge. The functional groups (-COOH) of acids will be disproportioned or will form anionic species (negative charge).

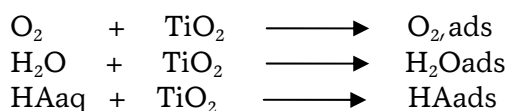


However, degradation of humic substance depend on surface charge of TiO₂. It is well known that the surface of TiO₂ is amphoteric and consequently, the charge of surface is pH-dependent. The pH pzc (the point of zero charge) is close to 6.3. The surface of TiO₂ have positive charge at pH lower than 6, and negative charger at the pH higher than 6. In this case, the adsorbtion of DOM on surface of TiO₂ will be very strong inhibited by electrostatic repulsion between similar charge, in this case negative charge. (Fig. 4). In acid condition, DOM will be adsorbed on surface of TiO₂.

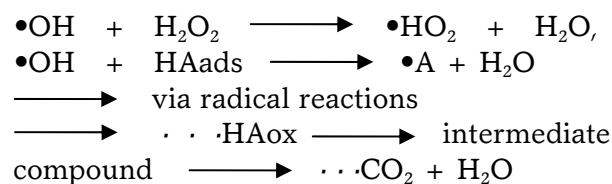
Degradation products of photocatalysis employing TiO₂ film catalyst

The measurement of degradation products by HPLC revealed that oxalic acid was detected consistently. Fig. 6 shows the time course of DOM decay and formation of oxalic acid as an intermediate compounds. The concentration of DOM was gradually decreased and significant levels of oxalic acid are generated as the time irradiation increased.

The OH radical bound to the semiconductor surface is a chemical equivalent to the surface trapped hole. The hydroxyl radical is able to react with almost all organic molecules thus initiate the oxidative degradation. On the other hand, since the photocatalytic oxidation reactions take place on the surface of the photocatalyst, the elementary reaction steps of humic acid (HA) on the TiO₂/water interface can be represented by the following equations [11].



Hydroxyl radical is an extremely powerful oxidizing agent with a redox potential of +2.8 V. The attack of the produced oxidants as •OH/ •HO₂ radicals may result structural changes via hydroxylation, decarboxylation and decyclization in humic acid molecule producing less hydrophobic and less adsorbing aromatic moieties. •OH radical reactions:



CONCLUSIONS

Photocatalytic degradation of DOM using TiO₂ catalyst film was investigated. The TiO₂catalyst film that formed on the surface of stainless steel plate was predominantly found to be in the anatase form.

Effect of TiO₂ catalyst could degrade DOM molecules. The degradation of at the solution in the presence of TiO₂ catalyst was faster than that in the absence of TiO₂

The degree of degradation of DOM in acid solution (63%) at pH 5 higher than that in basic solution (47%)at pH 7 and (13%) at pH 9. The determination of intermediate degradation products by HPLC revealed that oxalic acid was detected consistently.

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Table 1. d (Å) values from the measurement and interpretation TiO₂ synthetic crystal comparing with database.

Rutile	Anatase	Measurement results of the plates	The form of TiO ₂
3.25	3.52	3.5271	Anatase
2.49	2.38	2.3787	Anatase
1.69	1.89	1.8923	Anatase

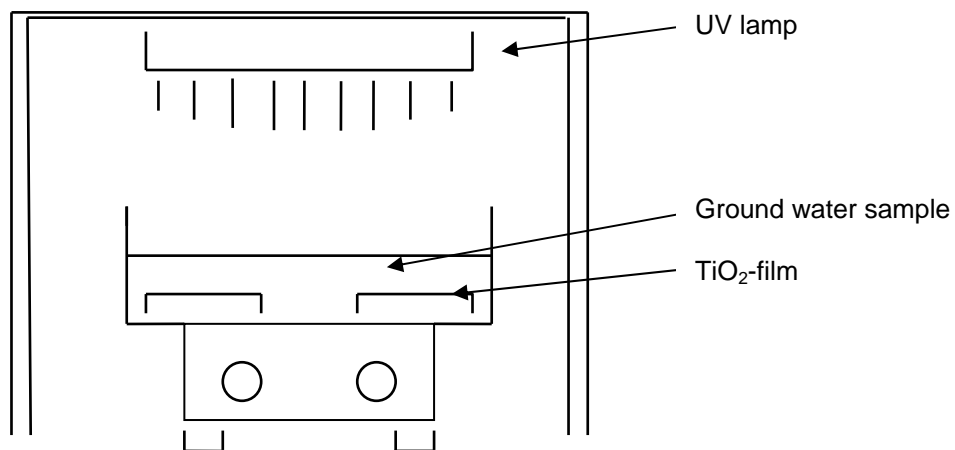


Fig. 1. Schematic of the photocatalytic reactor, comprised of a 2 x 10 W black light UV lamp (Toki, Japan), a pyrex glass vessel equipped with magnetic bar and catalyst sheets, and a magnetic stirrer.

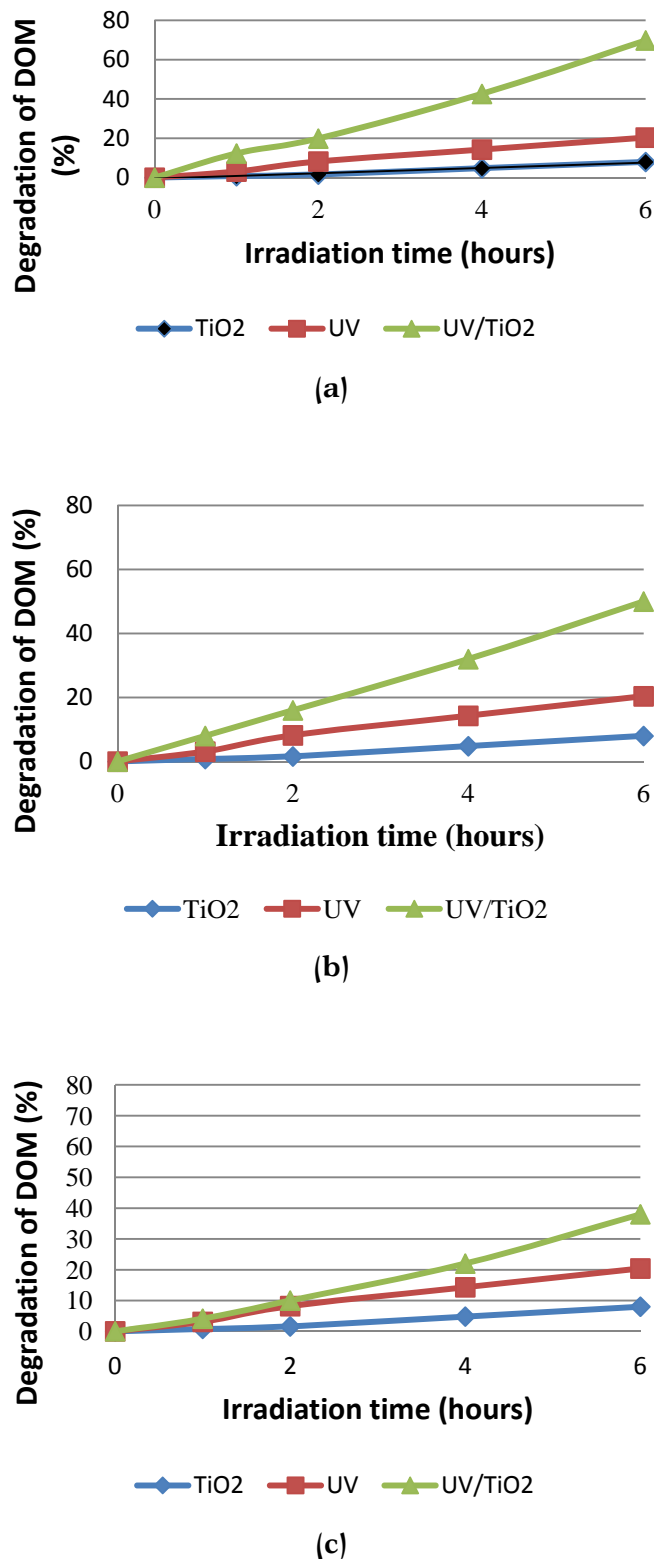


Fig. 2. Degradation of DOM due to photocatalytic, photolysis and control experiment. (a). pH 5 (b) pH 7 (c) pH 9

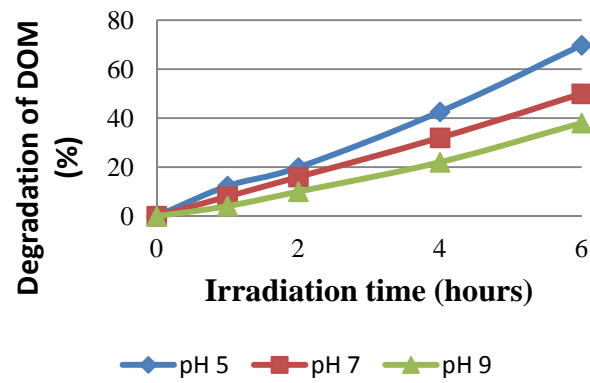


Fig. 3. Degradation of DOM during irradiation over TiO₂ film at different initial pH values (5, 7 and 9)

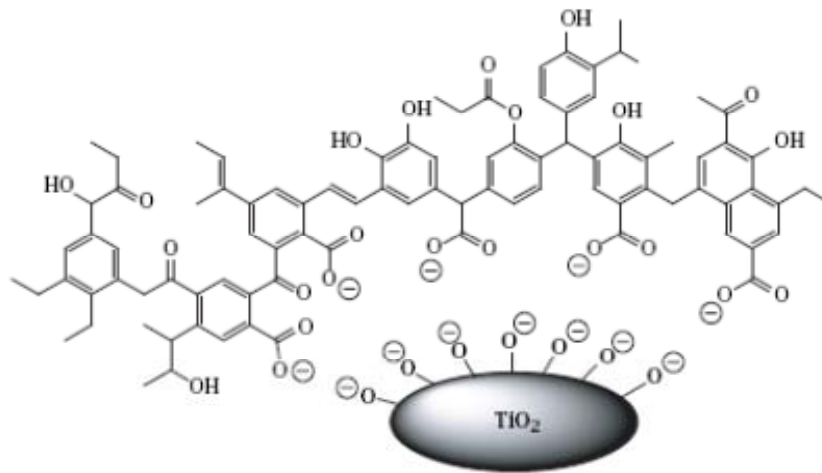


Fig 4. Repulsion effect of negative TiO₂ surface in alkalis condition [10]

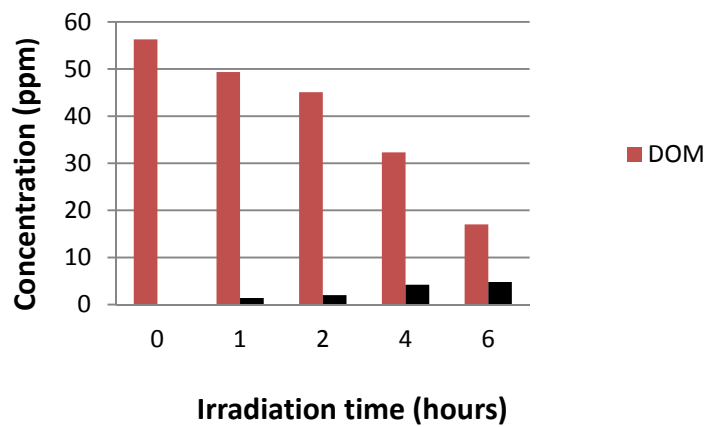


Fig. 5. Time course of DOM decay and formation of oxalic acid during photocatalysis on TiO₂ film

