

## TiO<sub>2</sub> BEADS FOR PHOTOCATALYTIC DEGRADATION OF HUMIC ACID IN PEAT WATER

Winarti Andayani\* and Agustin N M Bagyo

Center for The Application of Isotopes and Radiation Technologies, National Nuclear Energy Agency, Jakarta, Indonesia

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### ABSTRACT

Degradation of humic acid in aqueous solution containing TiO<sub>2</sub> coated on ceramics beads under irradiation of 254 nm UV light has been conducted in batch reactor. The aim of this experiment was to study photocatalytic degradation of humic acid in peat water. The irradiation of the humic acid in aqueous solution was conducted in various conditions i.e solely UV, in the presence of TiO<sub>2</sub>-slurry and TiO<sub>2</sub> beads. The color intensity, humic acid residue, conductivity and COD (chemical oxygen demand) of the solution were analyzed before and after irradiation. The compounds produced during photodegradation were identified using HPLC. The results showed that after photocatalytic degradation, the color intensity and the COD value of the solution decreased, while the conductivity of water increased indicating mineralization of the peat water occurred. In addition, oxalic acid as the product of degradation was observed.

**Keywords:** Peat water, humic acid, photocatalytic degradation, TiO<sub>2</sub>

### INTRODUCTION

Water resources from some regions in Indonesia such as Sumatera, Kalimantan and Irian Jaya contain a lot of humic Acid [1]. Humic acids (HA) are natural polymers, formed during degradation of plants and microbial materials. Humic acid contain aromatic blocks is characterized by a broad molecular weight distribution and high chemical heterogeneity. The acid has acidic character due to carboxylic and phenolic groups. That can be generally characterized as being yellow-brown [2]. The acids are the main constituents of the dissolved organic carbon (DOC) pool in surface waters (freshwaters and marine waters), and ground waters, commonly imparting a yellowish-brown color to the water system. Humic acid can influence the behavior of some pollutants significantly in natural environments, such as trace metal speciation and toxicity, solubilisation and adsorption of hydrophobic pollutants, and aqueous photochemistry. Humic acid can act as substrates for bacterial growth, inhibit the bacterial degradation of impurities in natural water, form a complex with heavy metals such as Fe, Pb, Mn making to be harder to remove them and transport the metals in the environment. Humic acid act as a source of methyl groups and thus react with hypochlorite ion which is used as a biocide in water treatment plants, to produce disinfectant by-products e.g., trihalomethanes, haloacetic acids, other chlorinated compounds and nitriles. Some of them are suspected to be carcinogenic [3-5].

Some conventional methods, e.g. coagulation, flocculation, and adsorption biofiltration have been applied in order to remove humic acids from water.

Disinfection of water containing humic acid using chlorine as disinfectant can produces organochlorins which are toxic compounds due to HA react with chlorine and cause hazardous disinfection by-products, e.g., trihalomethanes, haloacetic acids, haloacetonitriles [4-5]. Taking into account the disadvantages of these methods, the heterogeneous photocatalysis can be regarded as an effective alternative solution for the elimination of humic acid from aqueous solution [5-6]. Recently, heterogeneous photocatalytic degradation processes involving TiO<sub>2</sub> have been applied as an alternative showing a great potential for humic acid removal [7-9]. TiO<sub>2</sub> particle (anatase form) when was illuminated with light of wavelength  $\leq 380$  nm, produces excited-state electrons and hole pairs. The hole will interact with H<sub>2</sub>O which produce powerful oxidizing agent, hydroxyl radicals and superoxides [7]. Some researchers have examined on the photocatalytic degradation of humic acid and found that mineralization has occurred (7,10-12).

The use of slurry catalyst however creates a great technical problem in retrieving the catalyst from the treated water. In response to the retrieving problems many researcher have introduced an immobilized catalyst. This paper reported the study on photocatalytic degradation of humic acid in water using various TiO<sub>2</sub> (slurry and TiO<sub>2</sub> beads).

### EXPERIMENTAL SECTION

#### Materials

Peat soil was obtained from Pontianak, West Kalimantan, Indonesia, while the cation exchanger

\* Corresponding author.  
Email address : winlindu@batan.go.id

resin AG<sup>R</sup> 50 W-X 12, anion exchanger resin Biorex<sup>R</sup> 9, and the other materials such as sodium hydroxide, hydrochloric acid, methanol, ammonium iron (II) sulfate, potassium dichromate, silver sulfate, ferroin indicator, oxalic acid, acetic acid, propionic acid were obtained from Merck.

### Instrumentation

The experiments were conducted in batch reactor, with the size of 77 cm (length) and 24 cm (width). The TiO<sub>2</sub> beads were put in the batch reactor. Two of UV- C lamps tube ( $\lambda = 254$  nm, Philips) 30 watt having intensity of 1.8 mwatt/cm<sup>2</sup>, were positioned 1 cm from the bottom of the reactor.

Before and after irradiation the samples were analyzed. The parameters examined were humic acid residue, color intensity, COD values, conductivity of solution, and degradation products. Humic acid residue and color intensity in the solution were measured on Hewlett Packard Model 8453 Diode Array Spectrophotometer. The COD values were analyzed by chromat method [8]. Degradation products were analyzed using HPLC Shimadzu model LC-9A with shodex KC-811 column, equipped with UV detector at 210 nm, with, 0.005% phosphoric acid as eluent, and the flow rate were 1 mL/min.

### Procedure

#### Isolation of humic acid from peat soil

Sample preparations and treatments were done as follows: 500 mL of 0.5 N sodium hydroxide was added into a bottle containing 20 g of peat soil. The mixture was shaken for 4 h and then filtrated. The filtrate solution was then adjusted to pH 1, by adding 12 N hydrochloric acid. The precipitate was dissolved in 0.1 N sodium hydroxide. All of the filtrates were passed through columns containing anion and cationic exchanger resins. The solution of humic acid released from the column was ready to be illuminated.

#### Preparation of catalyst

The TiO<sub>2</sub> beads with the diameter of 0.4 cm were made from TiO<sub>2</sub> coated on ceramic. The ceramic was made of 40 g clay, 20 g kaolin and other material. All of the materials were blended well with the addition of water. The mixture was put into a pipe mold with 0.4 cm in diameter and 25 cm length. The ceramic was dried at 120 °C for 2-3 min and cut into small pieces, and continue heated at 800 °C for 3 h. Coating process was done by coated the ceramics in 20% of TiO<sub>2</sub> followed by dry processing at 700 °C for 5 min.

### Methods of irradiation

The photolysis and photocatalytic experiments were generally carried out by illumination. The source of light was 30 watt UV- C lamps tube ( $\lambda = 254$  nm) (Philips) 30 watt. The irradiation of humic acid (initial of color intensity and COD value were 578 PtCo and 109.1 ppm respectively) in aqueous solution were conducted at pH 7. Amount of 2 L sample were irradiated. The irradiations were conducted in various conditions, irradiation of humic acid without catalyst, in the presence of TiO<sub>2</sub> slurry and in the presence of TiO<sub>2</sub> beads (varied from 50 g up to 350 g). The irradiation time were ranging from 0 to 240 min. During irradiation, the solution of humic acid was aerated.

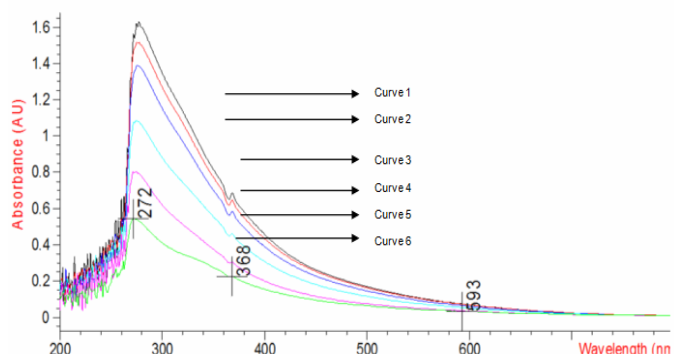
## RESULT AND DISCUSSION

### UV spectra of aqueous humic acid before and after irradiation

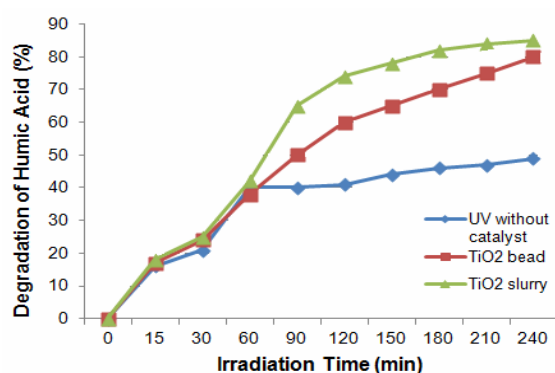
The humic acid in aqueous solution unirradiated shows a maximum absorption at 275 nm in the UV region as shown in Fig. 1, curve 1. The peak was assigned to be aromatic rings. After photocatalytic degradation mediated by TiO<sub>2</sub> bead under UV C irradiation, the intensity of the peak decrease gradually with the increase of irradiation time, (Fig. 1 curve 2 up to 6). After 240 min irradiation, the intensity of the peak almost disappear (curve 6). This implies that aromatic group in humic acid were destroyed by photocatalyst. OH radicals that formed from photocatalytic process attack the aromatic rings and resulting degradation products such as organic acids [6].

### Effect of TiO<sub>2</sub> catalyst on Degradation of humic acid

Fig. 2 shows plot of degradation of humic acid vs irradiation time at different treatment. The humic acid solution which is irradiated by UV in the absence of TiO<sub>2</sub> catalyst indicated that the humic acid molecules were degraded which increase gradually as the irradiation time. The same profiles were observed at the solution which is irradiated by UV in the presence of TiO<sub>2</sub>. Degradation of humic acid in photolytic process (irradiation in the UV without TiO<sub>2</sub>) could be achieved only about 50% after irradiation for 240 min. This could be explained as follows, humic acid could act as sensitizers or precursor for the production of reactive species such as singlet oxygen, humic-derived peroxy radicals, hydrogen peroxide, solvated electron, and •OH radicals. [9-10]. The reactive species formed in the solution might play as a major role in the degradation most of nonbiodegradable compound, even humic



**Fig 1.** UV spectral change of humic acid solution (50 mg/L, pH = 7) in the presence of TiO<sub>2</sub> bead as a function of irradiation time (curve 1 = unirradiated, curve 2 = 30 min, curve 3 = 60 min, curve 4 = 120 min, curve 5 = 180 min, curve 6 = 240 min)

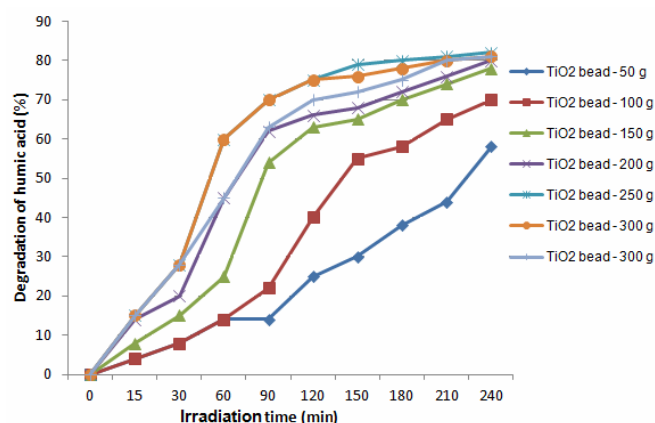


**Fig 2.** Degradation of humic acid after irradiated with UV at different time with and without catalyst

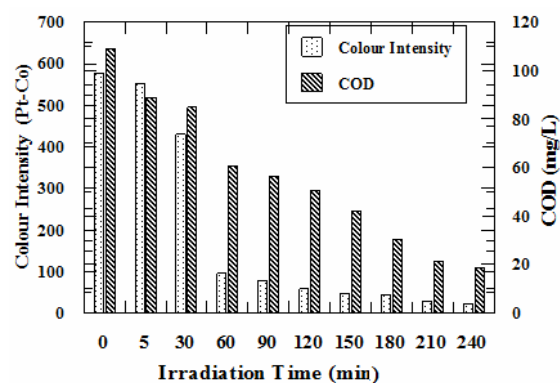
substances due to their ability to initiating photooxidation reactions.

Degradation of humic acid irradiated by UV light in the presence of TiO<sub>2</sub> catalyst (slurry and bead form) were faster than irradiated in the absence of TiO<sub>2</sub>. With the same time of irradiation, a significant reduction of humic acid by about 80% was observed. This case could be explained that species reactive in the solution are produced from humic acid itself which act as sensitizer and also from TiO<sub>2</sub> as catalyst.

In Fig. 2, also shown that the degradation of humic acid irradiated by UV light in the presence of TiO<sub>2</sub> slurry were faster than irradiated by UV light in the presence of TiO<sub>2</sub> bead. The explanation of this case are the surface area of TiO<sub>2</sub> bead which illuminated by UV light are smaller than TiO<sub>2</sub> powder. This related with the producing of species reactive in the solution. Although TiO<sub>2</sub> slurry have a better efficiency than immobilized ones to degrade humic acid, the separation of TiO<sub>2</sub> particles creates another problem to be solved in practical applications of the process. A major difficulty in the separation of TiO<sub>2</sub> particles from treated water arises



**Fig 3.** Degradation of Humic Acid in water after of irradiation using amount of TiO<sub>2</sub> beads



**Fig 4.** Color intensity and COD of humic acid solution before and after irradiation

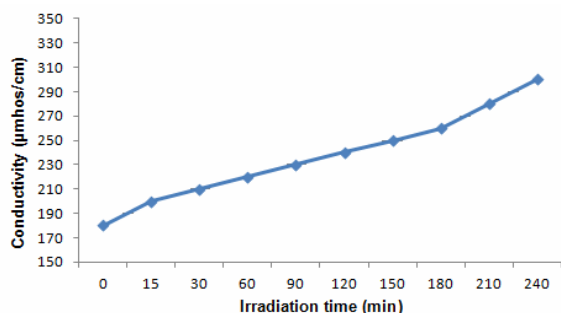
because TiO<sub>2</sub> particles are too fine to be removed by gravity settling.

#### Effect of amount of TiO<sub>2</sub> bead on Degradation of humic acid

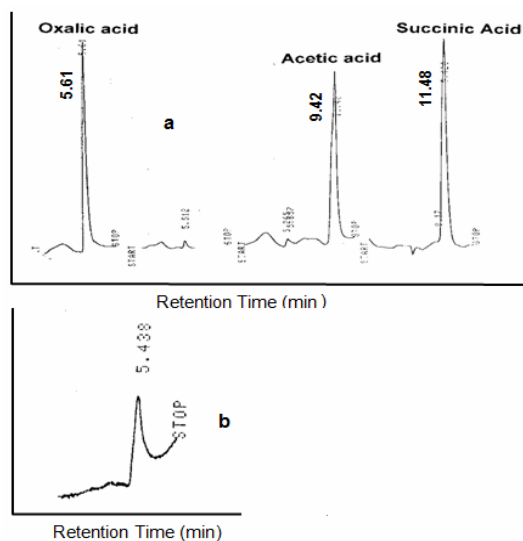
Fig. 3 shows plot of degradation of humic acid vs irradiation time at different amount of TiO<sub>2</sub> bead. The degradation of humic acid was increased with increasing the amount of TiO<sub>2</sub> bead under UV irradiation and reach constantly at the amount of TiO<sub>2</sub> bead more than 250 g. With the increasing of amount of TiO<sub>2</sub> bead, the surface area of TiO<sub>2</sub> in photocatalytic process was increased too. This related with the producing of species reactive in the solution.

#### Color intensity, COD value and Conductivity of humic acid solution

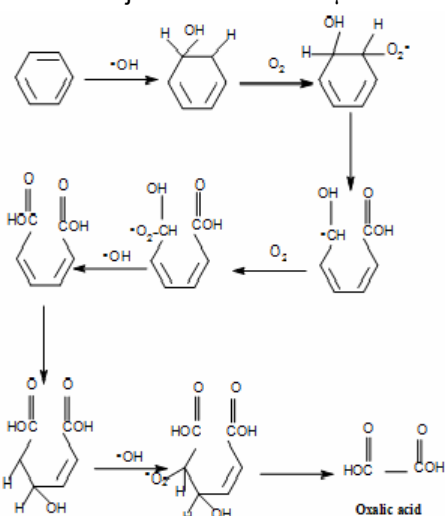
It is widely accepted that photocatalytic oxidation of organic compounds may produce organic acid, carbon dioxide, mineral acid, and water [13]. The color intensity and the COD values in the humic acid solution



**Fig 5.** Conductivity of humic acid solution before and after irradiation in the presence of 250 g TiO<sub>2</sub>-bead



**Fig 6. a.** Chromatogram of organic acid standard of 10 ppm oxalic acid, 200 ppm succinic acid, and 200 ppm acetic acid with the injection volume of 10 µL; **b.** Chromatogram of irradiated Humic acid in water at 240 min, with the injection volume 10 µL



**Fig 7.** Mechanism of photocatalytic degradation of aromatic ring in HA molecules

before and after irradiation in the presence of TiO<sub>2</sub> bead are displayed in Fig. 4. The COD values are the amount of organic substances contain in humic acid in solution. Fig. 4, indicated that the COD values decreased from 109.1 mg/L into 18.7 mg/L and color intensity decreased from 578 (PtCo) into 21 (PtCo) after 0 up to 240 min irradiation. Both the decreasing value of COD and color intensity are indicated that mineralization occurred due to degradation of humic acid.

The increasing of conductivity value during the photocatalytic of humic acid in water using amount of 250 g TiO<sub>2</sub> bead is displayed in Fig. 5. Fig. 5 shows that the conductivity of humic acid solution increase from 180 µmho/cm to 300 µmho/cm after irradiation for 0 up to 240 min. The increasing of the conductivity value indicated that mineralization of humic acid solution in water has occurred.

### Degradation product

The measurement of degradation products of humic acid solution after irradiation, was carried out by injecting samples into HPLC using Phenomenex C-18 column and solvent methanol/water : 1 : 9 at pH 4, with the flow rate of 1 mL/min. The chromatogram of organic acids standard is shown in Fig. 6a and irradiated humic acid in Fig. 6b. The irradiated humic acid arise peak that has a retention time of 5.61 min. The retention time of organic acid standards i.e oxalic acid, succinic acid, and acetic acid were 5.61, 9.428, and 11.48 min, respectively. By matching those two chromatograms it is assumed that oxalic acid was the degradation product that could be detected by HPLC. According to Kerck, the acid formation should be the major indication of the release of the acidic products. The photocatalytic degradation of HA lead to rapid elimination of color and this step caused the degradation of the aromatic structure. The mechanism of destruction aromatic ring is displayed in Fig. 7. The photocatalytic degradation leads to decreasing of the intensity of the peak in UV spectrum. This is mainly attributed to loss aromaticity by destroying of HA macromolecules.

### CONCLUSION

The photocatalytic degradation of humic acid in aqueous solution using TiO<sub>2</sub> bead and UV light as irradiation source was observed. It is clear that humic acid in peat water could be eliminated by photocatalytic degradation, resulted the decrease on color intensity and COD of solution and the increase of water conductivity. The formation of oxalic acid as the main product of photodegradation was observed.

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