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Degradation of Humic Acid as Peat Water Degradation Model by TiO$_2$Thin Layer Photocatalytic Reactor.

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ABSTRACT

Anatase TiO$_2$ has been successfully coated onto the surface of glass, aluminium, and ceramic supportsby screen printing techniques. The Surface layer was quite smooth with an average loading catalystfound to be 0.0222 g/cm^{2}andcoating thickness as 0.3μm on each surface of the support material. A thin layer of TiO$_2$ has proven worthy applied as a TiO$_2$ thin layer photocatalytic reactor-UV 365 nm irradiation to degrade humic acids that present in the water for a relatively long duration. Photocatalytic reaction for 20 hours makes humic acid in water degraded nearly 90 %. TotalOrganic Carbon (TOC) in water was decreased to 78 % and the pH of water became neutral from 6.6 to 7.1. Assumed thatthe formation of intermediates during the photocatalytic reaction and at the end of the process leading to the formation of mainly CO$_2$ and water. Photocatalytic reaction used TiO$_2$ thin layer on a ceramic support material and alumnium followsthe Langmuir Hinshelwood kinetics first order reaction,while on glass material support was analyzed to be pseudo-first order. The quantum yield found to be rangedfrom 9.9x10^{-3}to 1.3x10^{-2}mole/einstein.

Keywords: TiO$_2$ photocatalytic reactor, screen printing, degradation, humic acid, peat water

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INTRODUCTION

Peat water can be used as drinking and raw industrial water if it has been treatedto eliminate the chemicals content, especially humic acid. In many countries, before chlorination process, humic acidremoved from the water through coagulation using coagulant (aluminum sulfate or natural coagulant) and filtration. While coagulation process still leaves two major problems. The first problem is handling sludge residue with a high concentration of aluminum. The second problem requires close monitoring of the concentration of aluminum in water that has been processed which should not be more than 0.2 g/L in drinking water. During conventional water treatment process only 10-50 % TOC (total organic carbon) can be eliminated [1].

Another technology for removal of humic acid in water treatment has also been developed as an advanced oxidation [2,3], adsorption [4], ion exchange [5], reverse osmosis [6], biofilters [7], membrane processes [8]or degradation to eliminate humic acid in water by heterogeneous photocatalytic method TiO_2/UV [9-13].

Heterogeneous photocatalytic could be an effective alternative solution to eliminate humic acid from the peat water under reduced side effects. This process makes it possible to degrade the major organic molecules, without the addition of chemicals than photocatalyst (TiO_2 is the most popular) that can be activated by low-energy UV rays. UV light is used can be obtained from the UV light or artificial light.

There are several disadvantages of the TiO_2 suspension system, first is the low quantum efficiency due to UV radiation is not able to turn around the photocatalyst particles when the mixture is too murky, the second$TiO_2$is difficult to separated and regenerated from the solution phase, and the third is high dependency on pH conditions [14].

The coating of TiO_2 photocatalyst on the surface of the support such as ceramic, glass, plastic, PVC, paper with a thin coating of various techniques have been able to overcome the shortage of TiO_2 suspension system. Many researchers are optimistthat this technology economically viable, because it can take an advantage of a thin layer TiO_2 photocatalyst and low-energy UV light, as well as a thin layer TiO_2 photocatalyst can besimply regenerated. From the existing literature, the degradation of humic compounds in water, especially humic acid in peat water that has not been much enough to apply the TiO_2coated photocatalytic reactors.

Many techniques were found for coating photocatalyst onto the surface of the support material, where is one of which the most useful is sol-gel method with screen-printing techniques. Marcos, P Sao et.al (2008) have applied this technique in photocatalytic reactor design to eliminate the orange II color in water[15-17].Photoreactor consist of some commercial ceramic plates that coated with TiO_2 which arranged in orange II solution batch reactor. Visible light lamp 160 W was used as photon source and reactor temperature keep < 10^oC. Reactor photoactivity still low since only ceramic platecoated,but not for all the reactor surface.In the other hand cooling water system was required to keep reactor temperature remain constant.

Considering the facts above, the research has been carried out for the development a new photoreactor that all its surface totally coated with TiO_2 photocatalyst, effective light distribution, low cost, economy energy, and without temperature control. In this study thin film TiO_2 photocatalyst has been prepared by sol-gel method with screen-printing techniques. Anatase TiO_2 powder has beencoated on the surface of the glass, aluminum, and ceramicssupport to obtain a higher photocatalytic activity thin layer TiO_2 photocatalysts with high photocatalytic activity with a band gap corresponding to 365 nm UV light irradiation. These photocatalysts were efficient for the photocatalytic degradation of humic acid in aqueous solution, durable, and easily regenerated. This research is expected to be useful in the development of a new thin layer TiO_2 photocatalytic reactor as simple, effective, durable, and easy maintenance UV irradiation system in removal humic acid in water as a strategicpotential resource for drinking water, industry and tourism.

METHOD AND MATERIAL

Preparation and characterization of TiO_2 layer on the support

TiO_2suspension was prepared by dispersing anatase TiO_2 powder (GCE) and starch (Merck) in water with a composition (4:1:25, wt.%). TiO_2 suspension then ultraasonicated for an hour and coated to the surface of a catalyst support with screen printing technique (screen mesh 150T). Support which has all its surface coated with catalyst is then heated at a temperature of $120^{o}C$ for 1 hour. The weight of TiO_2thin layer produced simply determined gravimetrically.

The structure and size of the anatase crystalline TiO_2 photocatalyst respectively beforecoated, after coated (thin layer TiO_2 photocatalyst) and after photocatalytic reaction has been characterized by XRD (Bruker D8 Advance diffractometer, has a DSD software). The surface profile and the chemical composition of thin layers was determined by FESEM photo-EDX (JSM - 6701F). The specific surface area determined by nitrogen gas adsorption by TiO_2which measured by BET (Quantachrome Instrument Autosorb-1). Catalyst loading level determined gravimetrically. Absorbance profile of a thin layer TiO_2 photocatalyst and UV radiation attenuation is determined by DR-UV "Lambda 900" is a double-beam and double-monochromator spectrophotometer UV NISINIR. FT-IR equipment(Perkin-Elmer Infrared Fourier Transform) is used for the characterization of bonding Ti-O-Ti bonds and other existing vibrations in a thin layer of TiO_2 photocatalysts have been analyzed. All these results are compared to the experimental results of the characterization of uncoated thin layer photoreactor.

Photocatalytic Activity of TiO_2 Thin Film Photocatalyst Measurement

Humic acid solution in water is used to observed the activity of the photocatalytic degradation of TiO_2 thin film photocatalysts. Water containing humic acid that would be degraded by the photocatalytic TiO_2 thin film were prepared, namely a humic acid solution and a natural peat water samples. Stock solutions of humic acid (Fluka) 1000 ppm was prepared by

dissolving 1 g of humic acid powder in double distilledwater. Then the stock solution is filtered with a filter paper (Whatman No.1, UK) which had been weighed to remove suspended solids, and the filtrate stored at 4°C[16]. Filter paper and the residue is dried, cooled and weighed. Then recalculated more precise concentration of humic acid stock solution that had been made.

Activity ofTiO$_2$was determined by a degradation of 25 ppm humic acid under UV irradiation for 20 h in the photoreactor, as shown by Fig.1. All side of the support has been coated with a thin layer TiO$_2$ photocatalyst and was assembled as a container to be filled with humic acid solution, referred in this experiment to be a thin layer TiO$_2$ photocatalytic reactor. This reactor was placedinsidesealed container covered with aluminum foil to eliminate UV light absorptionby the container and reflected back the UV light to the photoreactor. UV emitted resulted from a Vilber Lourmat 12 watt lamp(VL-6.L) 365 nm placed within 10 cm on the surface of the water sample.
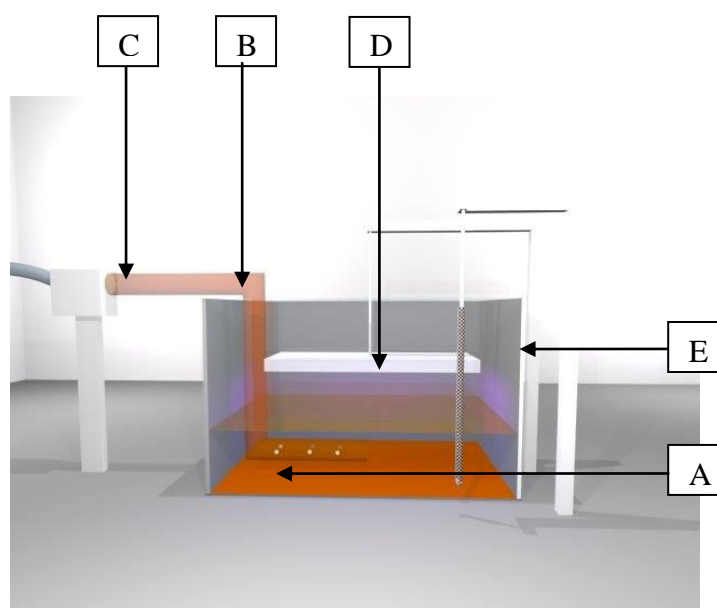

Figure1: Scheme of the reactor used for the photo catalytic process: A.thin layer ofTiO$_2$photocatalyticreactor; B. water containing humic acid; C. aerator pumps; D.UV lamp (Vilber Lourmat, VL-6.L 365nm), E. thermometer.

Then the water samples were irradiated every 4 hours. Changes in humic acid uptake was measured with a UV-Vis spectrophotometer (Analytikjena, Specord 200), then set up of the value of Total Organic Carbon (TOC) change and pH before and after degradation. In addition to the photocatalytic degradation process, the experiment was also conducted for the process of catalysis, photolysis and control (without catalyst and UV irradiation) with a reaction time of six hours.

RESULTS AND DISCUSSION

Characterization of TiO$_2$ thin film

XRD monitoring were carried out respectively on TiO$_2$powder and a thin layer before and after photocatalytic reaction showing certain crystalline peaks. In Fig. 2. shownsome peaks

with the highest intensity which appears at 2θ : 25.31 (101), and some supported peaks at 2θ : 36.94 ; 37.79 ; 38.63 ; 47.99 ; 53.87 ; 55.07. The following data are matched with reference to JCPDS No. : 04-0477 (D) ; No. : 86-1156 (C) revealed that the crystalline peaks are due to TiO_2 anatase structure and no crystalline rutile and brookite peaks were found. Trends are also not significantly different from the results observed in the XRD analysis of TiO_2 thin film which is coated on the support glass, ceramic and aluminum. It is concluded clearly that the support material does not affect the crystal structure of TiO_2 photocatalyst.
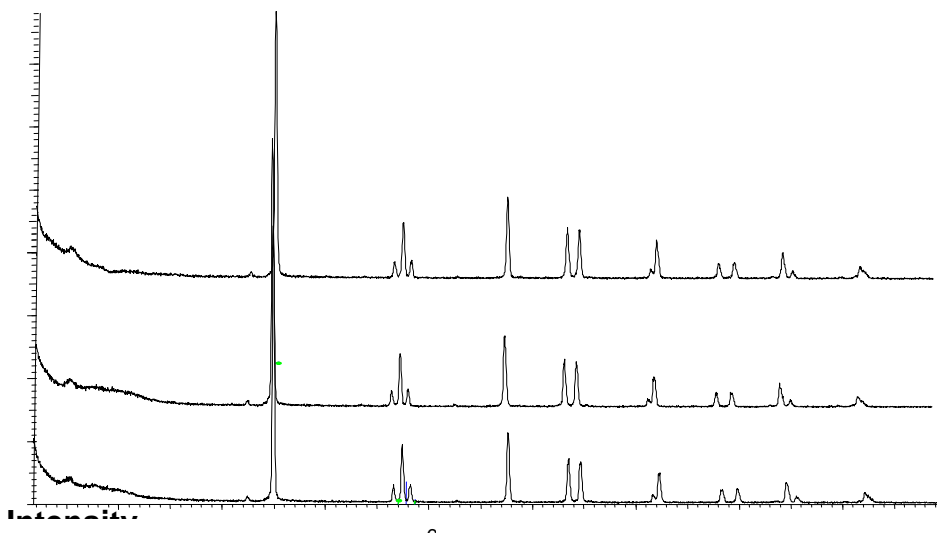

Figure 2: X-ray diffraction pattern of TiO$_2$ photo catalyst powder (a), a thin layer of TiO$_2$ on glass support before(b) and after photocatalytic (c).

Fig. 2. clearly shown that the sharpest widths peaks with narrow and highest diffraction at 2θ : 25.31 (101). The crystallite size can be determined by Scherrer formula by using diffraction pattern that has highest intensity. The crystal size of $TiO_2$of photocatalytic reactor before and after coating are35 nm, 35 nm and 33 nm, respectively. This value does not change significantly even though TiO_2coated on different supports.

Trend analysis results of XRD diffraction patterns did not significantly change during the photocatalytic processs, as where only anatase phase was found. Crystal size is slightly decreased but actually this condition is theoretically has an advantage corresponding expansion of the surface area. These results obtained are in accordance with the specific surface area of the data confirmed experimentally.

The specific surface area of$TiO_2$was characterized through a measurementby BET analyzer (Quantachrome Instrument Autosorb - 1). BET analysis results can be seen in Table 1. The data in Table 1. showed that the specific surface area of TiO_2 photocatalyst beforecoating is 9.5335 m^2/g and increased to 15 % after coating tocertain material support but not signicifantly changed during the photocatalytic process.

Table 1: BET data of TiO₂ before and after coating and used as a TiO₂thin layer of photocatalytic reactor

Parameter	TiO$_2$ before coating	TiO$_2$ after coating	TiO$_2$ after photocatalytic	Standard TiO$_2$ *)
BET surface area (m^2/g)	9.5335	10.9276	9.2268	7.6000
Total pore volume (cm^3/g)	0.03054	0.03410	0.02607	-
Pore size (nm)	6.8881	14.5067	13.6358	5.0000

*) A.Sclafani, L et al, 1990. *J. Phys.Chem*.94; 829

The similar condition was also foundin the porosity measurement of the TiO$_2$ photocatalyst. The total pore volume increased about 12 % after coating to the support material and not significantly changed after a series of application as a photocatalytic reactor. Coating process modified pore size of photocatalysts. TiO$_2$ thin layer pore size is 15 nm, tent to increase of more than twiceof TiO$_2$ powder pore. Photocatalytic process causes a thin layer of TiO$_2$ pore size change of only 6%.

These data confirm that the BET average pore diameter of a thin layer is anatase TiO$_2$ photocatalysts applied as a photocatalytic reactor is 11-15nm which is a TiO$_2$ mesoporous type (2-50 nm; IUPAC). Conditions favorable for mesoporous pore system can be controlled and can be applied widely for measuring the penetration of molecules between sub-nanomaterials and nanomaterial.

Surface profile of the porous layer of TiO$_2$ photocatalyst correspond to the FESEM images as shown in Fig. 3. Surface topography of a thin layer of porous TiO$_2$ confirm the results of BET analysis that is mesoporous TiO$_2$ thin film. The Surface layer is quite smooth with an average catalyst loading of 0.0222 g/cm^2 andcoating thickness about 0.3µm on each surface of the support material. The thickness of the layer should be regulated to obtain optimum photocatalytic degradation on the photocatalytic reactor apply a thin layer of TiO$_2$. Chang, et.al., 2000 [21], has degraded phenol in water and concluded that the optimum degradation occurs in a thin layer with a thickness of photocatalyst was <0.8µm.

SEM photograph showing the surface of the photocatalyst TiO$_2$ porosity on intra and inter- particle. The morphology of TiO$_2$ layer in the spherical granules form (spherical) with an average diameter of ±15-50 nm.These topography and morphology help the penetration of photons of UV irradiation inside entire surface of the catalyst layer. The more photons are adsorbed on the catalyst surface have more opportunities that lead to the formation of•OH radicals in a photocatalytic reaction. The electron and hole recombination of TiO$_2$ photocatalyst can be prevented and can improve the ability of photocatalytic reactor to degrade the organic molecules.

Differences surface morphology of thin film TiO$_2$ photocatalyst after the photocatalytic reaction occurs due to hydrolysis by humic acids that cause aggregation on TiO$_2$. Morphology in this study together, who investigated the influence of acid and alkaline hydrolysis on the photocatalytic activity and microstructures catalytic TiO$_2$ prepared by sol-gel method.
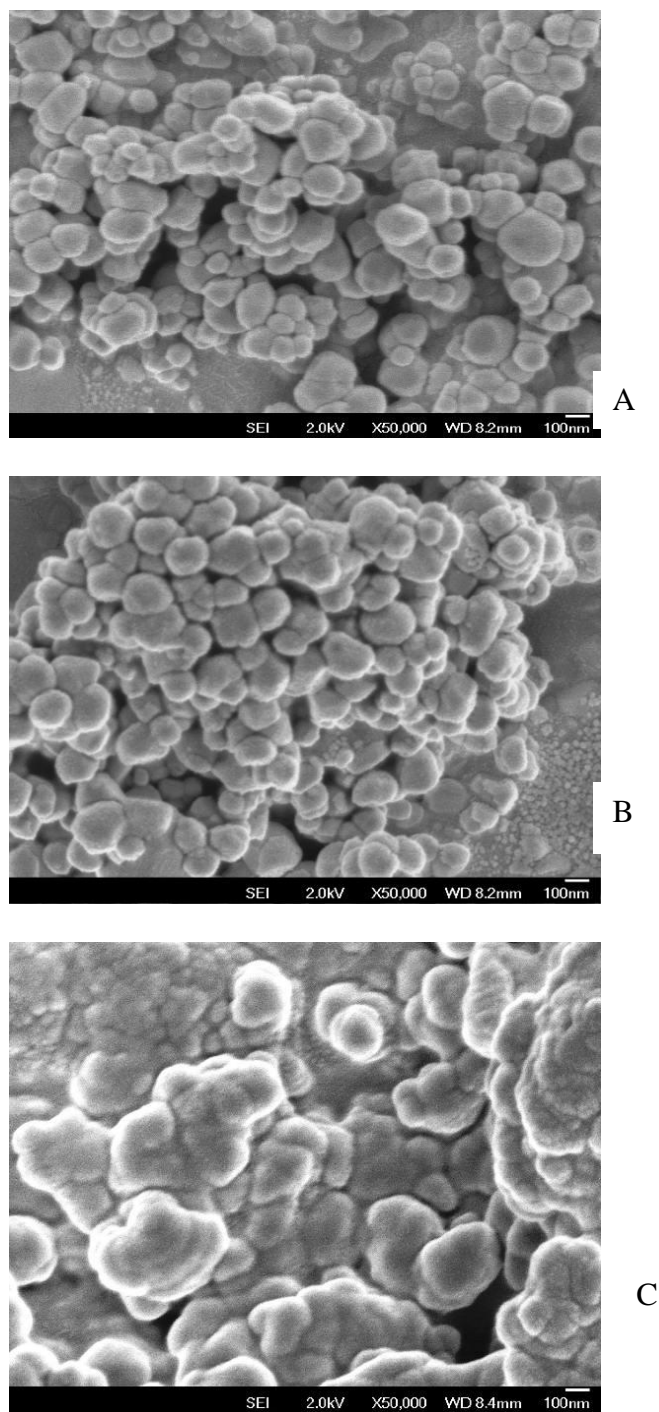
Figure 3: SEM imageof TiO$_2$photocatalyst. (a) beforecoating, (b) aftercoating, and(c) used photocatalyst.

To determine the presence of other elements that may diffuse on the surface of a thin layer of TiO$_2$ EDX analysis. Data EDX analysis results can be seen in Table 2. EDX results showed that only a thin layer of TiO$_2$ containing Ti and O. While C and Pt are read from the instrument sample comes from pengcoatingan process on sample analysis. The number of carbon element on the surface of a thin layer TiO$_2$ photocatalytic reactor after application show an increase of

approximately 15 %. This increase is due to the humic acid molecules or intermediate compounds which adsorbed on the surface of the photocatalytic TiO_2 thin layer reactor. This statement is also confirmed by the results correspond to the photocatalytic activity of humic acid degradation in water.

Table 2: Characterization results of TiO_2photocatalystcompositionwithEnergyDispersiveX-ray (EDX: FESEM-EDX)

Element	TiO_2 before coating		TiO_2 after coating		TiO_2 after photocatalytic		Standard TiO_2*)	
	% massa	keV	% massa	keV	% massa	keV	% massa	keV
Ti	66.40	4.508	67.02	4.508	58.40	4.508	48.18	4.508
O	22.77	2.048	22.02	0.525	28.92	0.525	28.30	2.048
C, Pt	10.83	0.277	10.96	0.277	12.68	0.277	-	-
*) Agus Santoso, et al. BATAN								

Photocatalytic degradation of humic acid

Photoactivity of thin layer reactor TiO_2on each of the support materials determined for 25 ppm of humic acid solution and peat water. A thin layer of TiO_2 photocatalytic degradation leads to loss of a yellowish brown color of humic acid solution. After photocatalytic degradation for 20 hours, humic acid solution becomes cleared. The results of the visual observation was later confirmed by theabsorption spectra of humic acid.
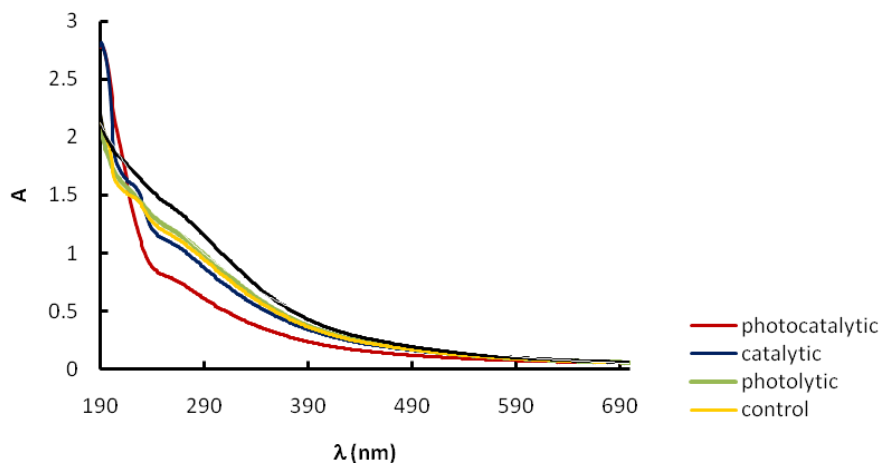

Figure 4: UV-Visible absorption of 25ppm humic acid after 6hours of the process at various operating conditions of a thin layer ofTiO_2 photo catalytic reactor.

UV-Vis analysis as shown in Fig. 4. provide the fact that the humic acid absorbance has beenhighly decreased in the UV region between 190-400 nm. Irradiation with UV,light absorbance decreased to 90 %. Quite significantly different from solution treated without light and catalyst (control), catalyst only, and the UV irradiated only. These results are correspond to the data obtained by Uyguner et al, 2005, which have concluded that the decline in the value of the specific absorbance caused by the degradation of humic acid into a compound that absorbs

less UV through a series of intermediate products [25]. It can be also explained that a thin layer TiO$_2$ photocatalytic process is very effective to degrade humic acids in comparison with catalytic or photolytic process.

Performance of the photocatalytic degradation of 25 ppm humic acid by a thin layer TiO$_2$ photocatalytic reactor on the support material as glass, ceramic, and aluminum for 20 hours irradiation is described in Fig. 5. In the Fig. 5a. seen that each reactor is able to degrade humic acids to approximately 80-90 % with almost the same degradation trend. Degradation increased sharply to 12 hours and then the reaction is only slightly increased to 20 hours of reaction. On the other hand the humic acid in the water after the photocatalytic degradation has been greatly reduced. It is evident from the increase in water pH from 6.6 to neutral (7.1 to 8.0). The profile of change of pH during the photocatalytic degradation shown in Fig.c.
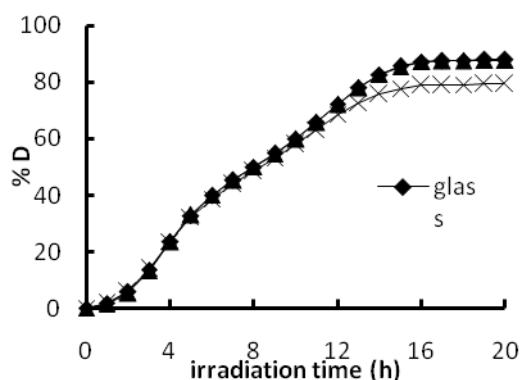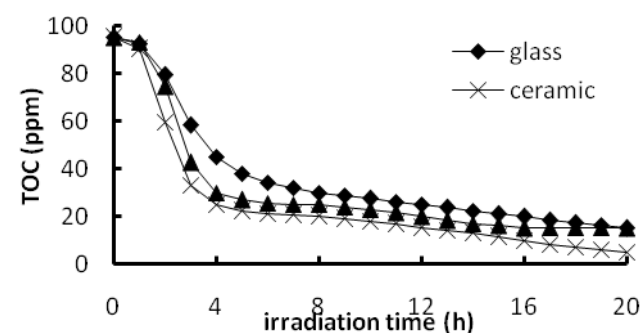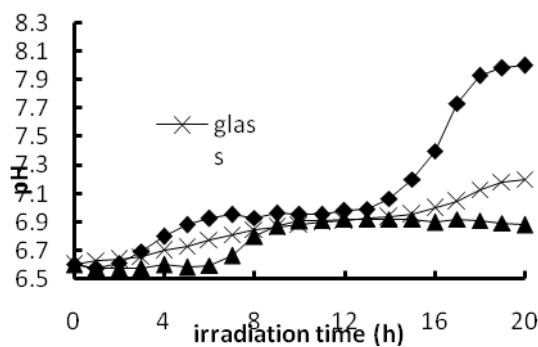

Figure 5.a

Figure 5.b

Figure 5. c

Figure 5: Degradation of 25 ppm humic acid in 20 h UV irradiation onto TiO$_2$ thin layer layer onthe supportglass, ceramic, and aluminum. 5.a) % Degradation changes, 5.b) total organic carbon (TOC) changes, 5.c). pH changes.

The results of this degradation is associated with a decrease in the total number of organic carbon (TOC) as shown in Fig. 5b. at the beginning of the photocatalytic degradation observed that TOC only changed slightly but subsequently showed a sharp decline. The sharp decline TOC value is thought to be caused by the adsorption of humic acid on the surface of the photocatalyst. Increased of TOC due to the release of intermediate oxidation products from the surface of TiO$_2$ photocatalyst into solution. It is also reported by Huang et al[27] which states that

humic acid adsorbed on the photocatalyst surface is oxidized and transformed into intermediate oxidation products which are more hydrophilic than the humic acid. The decrease in TOC values also indicate mineralization of intermediate products of humic acid degradation into carbon dioxide and water, as has also been observed.

In this study observed that the possibility of humic acid adsorption on the surface of the photocatalyst TiO_2 and intermediate products were determined by comparing the FTIR spectra of TiO_2 photocatalyst with humic acid spectra. Fig. 6. shows the FTIR spectra before coated TiO_2 photocatalyst, TiO_2 thin layer, a thin layer of TiO_2after contacted with humic acid, a thin layer of TiO_2 after contacted with humic acid and UV irradiated , and humic acid spectra. The vibration frequency of for TiO_2 photocatalyst was detected in the fingerprint region between 800-400 cm$^-$^{1}. This vibration peak indicate character of Ti - O- Ti bonding. Once the character coated TiO_2 photocatalyst vibrational peaks are not so changed OH stretching vibration only slightly expanded, indicating that there is still a water molecule is not lost due to heating during coating process.
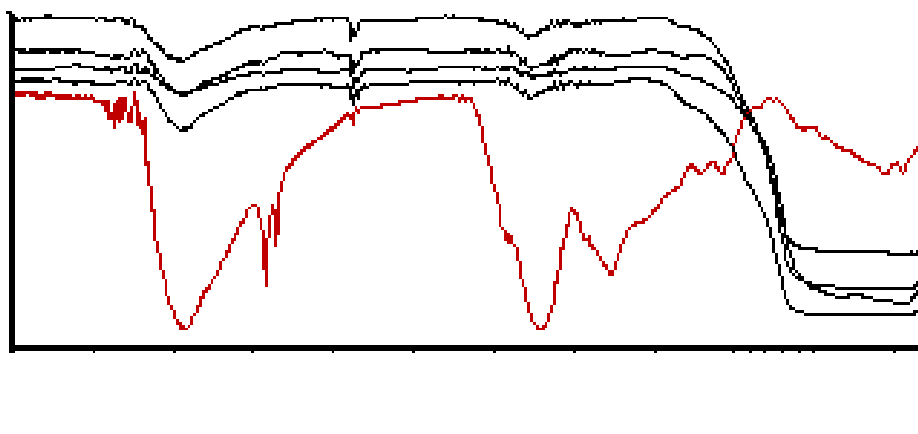

Figure 6: FTIR spectra of TiO_2 photocatalyst and humic acid. a) TiO_2, b) TiO_2 thin layer, c) TiO_2 thin layer absorbed by humic acid, d) TiO_2 thin layer after humic acid photocatalytic reaction, e) humic acid.

There are five new vibrational peak after TiO_2thin film contacted with humic acid which gives the information that there is a carbonyl group leading to carboxylic acids, besides that there is also a bonding alkyl - CH_3 and - CH_2- . The data obtained can be concluded that there is a carbonyl group in the form of long chain carboxylic acids adsorbed on the surface of TiO_2 photocatalyst. During photocatalytic TiO_2 coating degraded into molecules of humic acid intermediates such as carboxylic acid molecule with a carbon chain length is evident from the vibration peak -CH bonds. This assumption is connected with the information that five new vibration detected when a thin layer of TiO_2 in contact with humic acid peak only C-H stretching vibration frequency at 2920 cm^{-1} is read when the TiO_2 film contacted with humic acid irradiated with UV for 20 hours. Frequency vibrations appear on the 665 cm^{-1} which is the vibration of the CO_2 molecule. From the above set of facts can be assumed that humic acids are degraded by photocatalytic TiO_2 thin film reactor produces intermediates are oxidized to CO_2 and water. These products also disinfect water in addition to purify water from molecules that

are harmful to living things and the environment. These results are even better when applied to the peat water with the same degradation trend.

The reaction rate of photocatalytic degradation in TiO_2 photocatalyst surface generally follows the Langmuir Hinshelwood following equation:

$$\ln (C_o / C_t) = k.t$$

The first order rate constant (k) obtained by plotting $\ln C_o/C_t$ versus t (irradiation time), and the subsequent determination of the value of k' using linear regression. Plots of $\ln (C_o/C_t)$ versus t (time) obtained in this study as shown in Fig. 7, while the % degradation, the half-life, and the value of the reaction rate constants of humic acid photocatalytic degradation by TiO_2 thin film reactor on each material support that shown in Table 3.
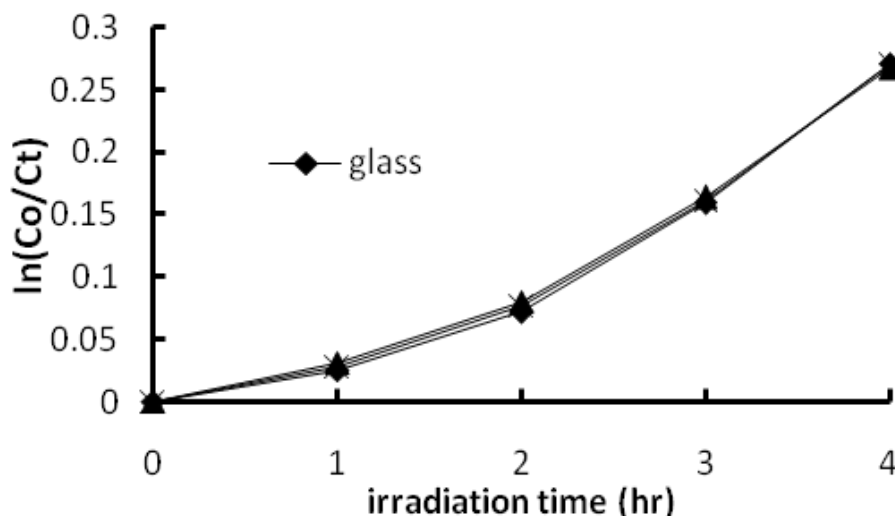

Figure 7: Ln (Co/Ct) and irradiation time plotting from 25ppm humic acid in aqueous solution and peat water after 20hours UV irradiation ontoTiO₂ thin layer on the support glass, ceramic, and aluminum.

The data in Table 3 explains that the humic acid photocatalytic degradation in TiO_2 photocatalytic reactor with the support material respectively of ceramic and aluminum follows the Langmuir Hinshelwood kinetics. Photocatalytic reaction can occurs gradually or consecutively and a first order reaction. As for the glass support material shows the non linear correlation coefficients, which means in consequent not a first order reaction. However, if the reaction in the early minutes of the negligible degradation reaction is first order reaction. From these facts it can be concluded that humic acid photocatalytic degradation by thin film TiO_2 photocatalytic reactor with glass support material is to be a pseudo first order reaction.

Table 3:Kinetics data of photocatalytic degradationfor 25ppm humicacid in aqueous solution and peat water after 20hoursUVirradiation ontoTiO$_2$ thinlayer onthe supportglass, ceramic, andaluminum.

Support	Degradation (%)	k (menit^{-1})	t$_{1/2}$ (menit)	R^2	Quantum Yield (mol. Einstein^{-1})
glass	88.00	0.057	12.158	0.903	1.3 . 10^{-2}
ceramic	79.43	0.058	11.948	0.916	1.7 . 10^{-2}
aluminium	87.80	0.058	11.948	0.928	9.9 . 10^{-3}
sampel	87.88	0.058	11.948	0.623	1.3 . 10^{-2}

In the initiation step of TiO$_2$ photocatalytic reaction on the support material glass, where is formed radicals that reacts with humic acid molecules are adsorbed on the catalyst surface. Since the more sufficiently contact time lead to the formation of more intermediates, so it gives the skin effect that blocks the degradation process.

Photochemical reactions quantum yield (Φ) is usually used to determine the efficiency of the photodegradation of pollutants. Where is the value of the quantum yield of the photocatalytic degradation of humic acid with a thin layer TiO$_2$ photocatalytic reactors obtained around 9.9.10^{-3} - 1,3.10^{-2} mole/Einstein.

CONCLUSION

The anatase TiO$_2$ has been successfully coated onto the surface of the various support materials such as glass, aluminum, and ceramics by screen printing techniques. The characterization results given an information that the resulting film is really mesoporous TiO$_2$. The Surface layer is quite smooth with an average loading catalyst found to be 0.0222 g/cm^{2}andcoating thickness around 0.3μm on each surface of the support material. A thin layer TiO$_2$ has proven worthy applied as a TiO$_2$thin layer photocatalytic reactor - UV 365 nm irradiation system to degrade humic acids contents in the water for a relatively long duration. Photocatalytic reaction for 20 hours makes humic acid in water degraded nearly 90 %.TOC in the water decreased to78% and the water became neutral. Assumed thatthe intermediates formed during the photocatalytic reaction and at the end of the process leading to the formation of CO$_2$ and water. Photocatalytic reaction used TiO$_2$ thin layer on ceramic material support and alumnium follow Langmuir Hinshelwood kinetics first order reaction, while the glass material support to be prseudo-first order reaction. The quantum yield of the reaction ranged from9.9.10^{-3}–1.3.10^{-2} mole/einstein.

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