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SYNTHESIS AND CHARACTERIZATION OF FILMS TIO$_2$FOR SOLAR UV-TIO$_2$ PHOTOCATALYTIC REACTOR

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ABSTRACT

Peat water can be used as drinking and raw industrial water if it has been treated to eliminate the chemicals content, especially organic carbon. In this research, heterogeneous photocatalytic by TiO_2 photocatalyst could be an effective alternative solution to eliminate total organic carbon from the peat water under reduced side effects. TiO_2 films as a photocatalyst synthesized by screen-printing technique was achieving 0.0053 mg/cm^2 TiO_2 loading. The characterization for the physicochemical properties of photocatalysts carried out by X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA) and Scanning Electron Micrograph (SEM). The smooth enough surface TiO_2 anatase film was showed by SEM and the film thickness ± 0,175 µm on glass support. XRD analysis conducted on TiO_2 photocatalyst powder inform the thin layer of photocatalytic TiO_2 before and after shows only the peaks of crystalline anatase with an average crystal size of 142 nm . The results show that the specific surface area of photocatalytic TiO_2 before coating 11.786 m^2/g and increased 134 % after coated to support the glass but did not significantly change during the photocatalytic process. TiO_2 film was success applied as solar UV-TiO_2 photocatalytic reactor to degrade total organic carbon (TOC) in peat water for long time duration. TOC was degradated as 94 % after irradiation for 6 hours and water became neutral.

Keywords: photocatalytic, TiO_2, solar reactor, total organic carbon, peat water.

1. INTRODUCTION

Indonesia has the largest tropical peat areas in the world, estimated at between 27 million hectares (50 % of tropical peat land area); in Sumatra 8.9 million hectares, 6.3 million hectares of Kalimantan and Papua 10.9 million hectares, as well as a bit on Halmahera and Sulawesi. Lodging in West Sumatra's peat swamp areas are in coastal areas, such as Kabupaten Pesisir Selatan, Padang Pariaman, Agam and in the northern part of the city of Padang[1]. The above data makes us aware of the magnitude of the water potential in Indonesia's peat lands.

Indonesian communities that living in peat land for generations have used the land for agriculture, livestock and fisheries. Despite the favourable economically but in terms of public health in peat land threatened the negative impacts of water consumed peat.

Peat water does not meet the requirements of clean water that has been set by the Ministry of Health Republic of Indonesia caused by its brown colour, smelled dreadful, and acidic. The brown colour comes from peat water humic substances (humic substances = HS) contained in soil and peat. HS include the fraction of humic acid, fulvic and humin.

The functional group owned humic acid causes humic acid in aquatic systems can form complexes with heavy metals and organic pollutants such as pesticides, insecticides and herbicides. Wang *et al.* suggested that humic acid is also a precursor mutagenic product[2]. Research Eggins *et al.* showed that humic acid reacts with chlorine in existence for water disinfection process to produce carcinogen organochloride compounds[3].

Peat water can be used as drinking and raw industrial water if it has been treated to eliminate the chemicals content, especially humic acid. In many countries, before chlorination process, humic acid removed from the water through coagulation using coagulant (aluminium 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 aluminium. The second problem requires close monitoring of the concentration of aluminium 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) that can be eliminated [4].

Another technology of removal of humic acid in water treatment has also been developed as an advanced oxidations [5],[6], adsorption[7], ion exchange[8], reverse osmosis[9], ozonation, biofilters[10], membrane processes [11] or degradation of humic acids by homogeneous photocatalytic reaction (superchlorination, hydrogen peroxide). Bekbolet, M, *et al.* has been developed a series research to eliminate humic acid in water by heterogeneous photocatalytic method TiO_2/UV[12-14].

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 solar light or artificial UV light.

Research on the utilization and development of heterogeneous photocatalytic processes TiO_2/UV for the removal of humic acid has been published[12-14]. The photocatalytic reaction previously was carried out in a TiO_2 suspension system for all the publications. 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 [15].

The coating of TiO_2 photocatalyst on the surface of the support such as ceramic, glass, plastics, PVC, paper with a thin coating of various techniques have been able to overcome the shortage of TiO_2 suspension system. Many researchers are optimist that 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 be simply regenerated [16], [17]. 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.

By applying the TiO_2 photocatalytic reactor batch which has immobilized on a glass support and UV rays coming from 365 nm UV lamp humic acid as a model compound in water have been successfully degraded peat up to 90 % [18]. Development of photocatalytic reactors is done by varying the catalyst support material such as glass bead[19], glass, ceramics and aluminum. To obtain an effective thin layer of photocatalytic TiO_2, immobilization of TiO_2 on the surface of the catalyst support made with a method using a sol-gel technique of dip-coating and screen-printing[20-21]. The photocatalytic reactor that is used each using UV irradiation comes from the UV lamp meaning they require electricity. Indonesia has experienced in electricity crisis on the other hand the potential for abundant sunshine in Indonesia can be optimized as a source of UV light irradiation.

In this research, a model of the entire solar photocatalytic reactor in the reactor surfaces had been coated with TiO_2 photocatalyst, light distribution that is effective and without temperature control. In this study, a thin layer of photocatalytic TiO_2 was prepared by sol-gel method with screen-printing technique. Anatase TiO_2 powder is coated on the surface of the glass support to obtain a thin layer of photocatalytic activity of TiO_2 photocatalyst with a higher and a band gap of 3.2 eV corresponding to a UV light irradiation from sunlight. The photocatalyst is efficient enough to photocatalytic degradation of humic acid in peat water and can be regenerated.

This study is useful in developing a new thin layer of solar TiO_2-UV photocatalytic reactor were simple, effective, durable, and UV irradiation system of sunlight that is maintained in removing humic acid present in water. The results of this research become potential and strategic solutions to transform peat water into a new source of clean water, drinking water, raw water for industry (particularly the agro industry) and tourism.

2. MATERIALS AND METHODS

General procedure

a) Peat water sampling

The peat water samples of to be degraded by TiO_2 photocatalytic reactor models taken in the area of Siak -Riau namely in the Siak River, in the area around the pulp and paper industry as well as in the plantation areas near community settlements.

b) Preparation and characterization of TiO_2 layer on the support

The TiO_2suspension was prepared by dispersing anatase TiO_2 powder (GCE) and starch (Merck) in water. TiO_2 suspension then ultra sonicated for an hour and coated to the surface of a catalyst support with screen printing technique (screen mesh 150T). Support which all it surface has coated with catalyst is then heated at a temperature of 120 ^oC for 1 hour. The weight of TiO_2 thin layer produced simply determined gravimetrically.

The structure and size of the anatase crystalline TiO_2 photocatalyst respectively before coated, 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. 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. The thermal stabilities were measured using Thermal Graviemtric Analysis (TGA/SDTA). All these results are compared to the experimental results of the characterization of uncoated thin layer photoreactor (control).

c) Photocatalytic activity of TiO_2 thin film photocatalyst measurement

The Activity ofTiO_2 thin film photocatalysts that have been prepared determined by degraded the peat water under UV irradiation for six hours in the solar photoreactor, as shown by Figure-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 peat water that contain humic acid, referred in this experiment to be a thin layer TiO_2 photocatalytic solar reactor. Then the water samples were irradiated every 1 hour. Changes in humic acid uptake was measured with a UV-Vis spectrophotometer, and then set up of the value of Total Organic Carbon change (TOC) 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).

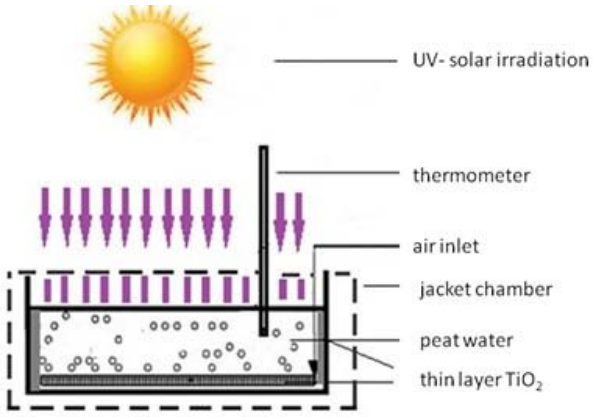


Figure-1. Scheme of the solar reactor used for the photocatalytic process.

3. RESULT AND DISCUSSION

a) Quality of peat water

The peat water is yellow brown water as shown in Figure-2, acidic with pH, total organic carbon (TOC), dissolved oxygen (DO) average gained consecutively as follows 5.4; 207 mg/L; 2.3 mg/L, respectively.

Figure-2. Peat water sampling condition.

b) Synthesis TiO_2 thin film

A thin layer of TiO_2 photocatalyst most optimum is obtained when prepared from TiO_2 suspension and starch in water at a ratio (4:1:25) wt. % was coated by screen printing technique.

c) Characterization TiO_2 thin film

XRD monitoring was carried out respectively on TiO_2powder, a thin layer before and after photocatalytic reaction showing certain crystalline peaks. Figure-3. Shown some 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 revealed that the crystalline peaks are due to TiO_2 anatase structure and no crystalline rutile and brookite peaks were found.

Figure-3 clearly shown that the sharpest widths peaks with narrow and highest diffraction at 2θ: 25.31 (101). The crystal size of $TiO_2$of photocatalytic solar reactor before and after coating are 139,97 nm; 148,00 nm; 138,00 nm, respectively. Trend analysis results of XRD diffraction patterns did not significantly change during the photocatalytic processes, 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[22]. These results obtained are in accordance with the specific surface area of the data confirmed experimentally.

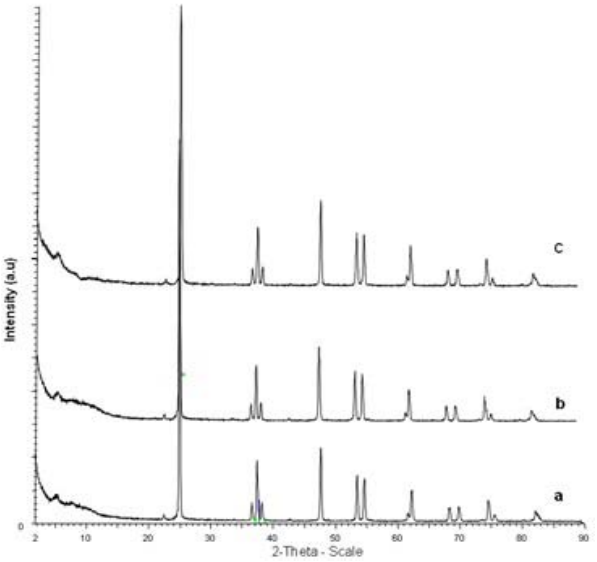


Figure-3. X-ray diffraction pattern ofTiO_2 photocatalyst powder(a), a thin layer ofTiO_2on glass support before(b) and after photocatalytic(c).

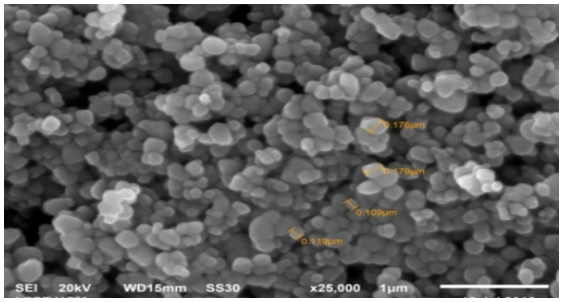
The specific surface area of TiO_2 was characterized through a measure by BET analyzer (Quantachrome Instrument Autosorb - 1). BET analysis results can be seen in Table-1. Shown the data that the specific surface area of TiO_2 photocatalyst before coating is11,786 m^2/g and increased to 134 % after coating to certain material support but not significantly changed during the photocatalytic process.

The similar condition was also foundin the porosity measurement of the TiO_2 photocatalyst. The total pore volume increased about 10 % 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 4 nm, tent todecrease of more than twiceof TiO_2 powder pore. Photocatalytic process causes a thin layer of TiO_2 pore size increase of 64%.

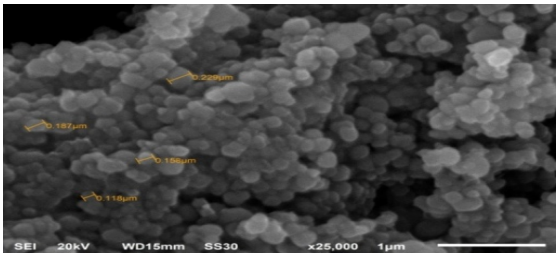
Table-1. BET data of TiO_2 before and after coating and after usedasa solar TiO_2-UV photocatalytic reactor.

Parameter	TiO_2 before coating	TiO_2 after coating	TiO_2 after photocatalytic
1. BET surface area (m^2/g)	11,786	27,617	16.370
2. Total pore volume (cm^3/g)	0,05023	0,05499	0.05368
3. Pore size (nm)	8,5242	3,98261	6,55687

These data confirm that the BET average pore diameter of a thin layer is anatase TiO_2 photocatalysts applied as a photocatalytic reactor is 6-8 nm 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.



(a)



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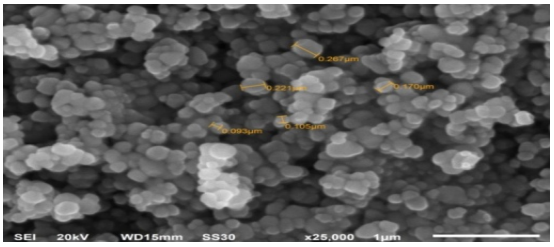
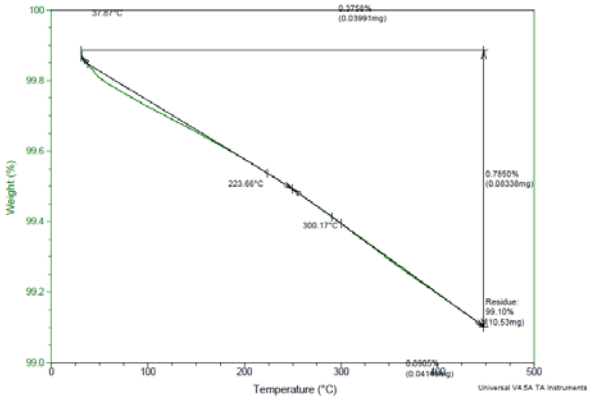


(c)

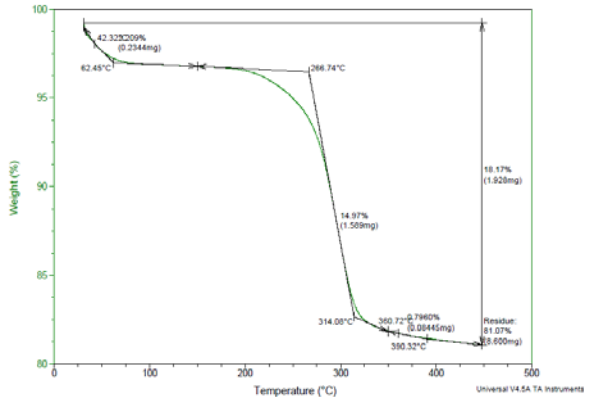
Figure-4. SEM images (25.000X) of TiO_2 photocatalyst. (a) before-coating, (b) after- coating, and(c) used potocatalyst.

Surface profile of the porous layer of TiO_2 photocatalyst correspond to the FESEM images as shown in Figure 3. Surface topography of a thin layer of porous TiO_2 confirms the results of BET analysis that is mesoporous TiO_2 thin film. The Surface layer is quite smooth with an average catalyst loading of 0.053 g/cm^2 and coating thickness about 0.175µm on each surface of the support material. The thickness of the layer should be regulated to obtain optimum photocatalytic degradation on solar TiO_2-UV photocatalytic reactor that applied a thin layer of TiO_2. Chang, *et al.* has degraded phenol in water and concluded that the optimum degradation occurs in a thin layer with a thickness of photocatalyst was <0.8µm[23].

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 ±0,2 µm. 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 holes recombination of TiO_2 photocatalyst can be prevented and can improve the ability of photocatalytic reactor to degrade the organic molecules.



(a)



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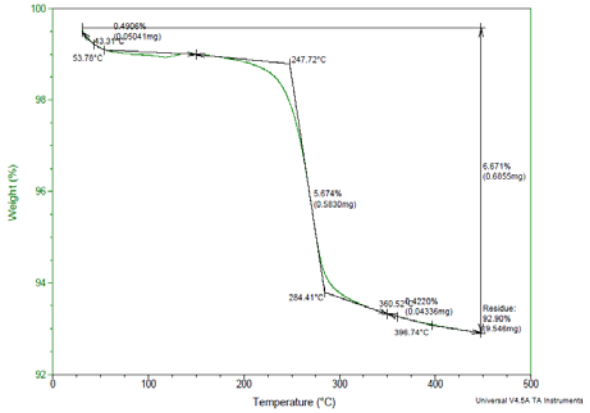

(c)

Figure-5. TGA/SDTA images of TiO_2 photocatalyst. (a) before-coating,(b) after- coating, and(c) used photocatalyst.

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 with the resulting J. Yu *et al*., 2003, who investigated the influence of acid and alkaline hydrolysis on the photocatalytic activity and microstructures catalytic TiO_2 prepared by sol-gel method [24]. Conclusion Yu *et al* also been reinforced by the results of research conducted by Miki Kanna, 2008, to a mixture of amorphous and nano-crystalline TiO_2 [25].

To determine the presence of other elements that may diffuse on the surface of a thin layer of TiO_2 EDX analysis. 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 coating 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 that similar to research result of Sun, D.D *et al.*, 2012 [26]. This statement is also confirmed by the results correspond to the photocatalytic activity of humic acid degradation in water.

The influence of temperature on the resulting thin layer was analyzed by TGA/SDTA, result can be seen in Figure-5 below. TGA/SDTA pattern in Figure-5a shows two endothermic peaks which is the peak decomposition of a thin layer TiO_2. The first area is the decomposition of the solvent than adsorbed on titania surface due to resulting in average weight loss of about 1 %. The second area declared peak decomposition of organic components (residual starch) contain in a thin layer TiO_2 so that the weight loss about 7%. The residue of the sample is TiO_2. This data confirm that the TiO_2 films are relatively stable against the reduction in mass due to the heat. These results were more pronounced with TGA/SDTA for photocatalyst coating before and after use as solar photocatalytic reactor as in the Figure-5 b and c.

Photocatalytic activity of TiO_2 thin film as a solar TiO_2-UV photocatalytic reactor

A thin layer of TiO_2 photocatalytic degradation leads to loss of a yellowish brown-colour of humic acid solution. After photocatalytic degradation for 6 hours, peat water becomes clear. The visual observation result confirmed by the absorption humic acidspectra.

FTIR spectroscopy analysis shows in Figure-6. Showing the fact that the humic acid absorbance has been highly 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[27]. 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.

It is evident from the increase in water pH from 5.4 to neutral (7.1 to 8.0). The degradation results associated with a decrease in the total number of organic carbon (TOC). Photocatalytic reaction for six hours makes TOC in the water decreased to94%. The decreased of TOC values also indicate mineralization of intermediate products of humic acid degradation in peat water into carbon dioxide and water.

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. Figure-6. Shown the FTIR spectra before coated TiO_2 photocatalyst, TiO_2 thin layer, a thin layer of TiO_2 after 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 indicates character of Ti - O- Ti bonding. Once the character coated TiO_2 photocatalyst vibration 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.

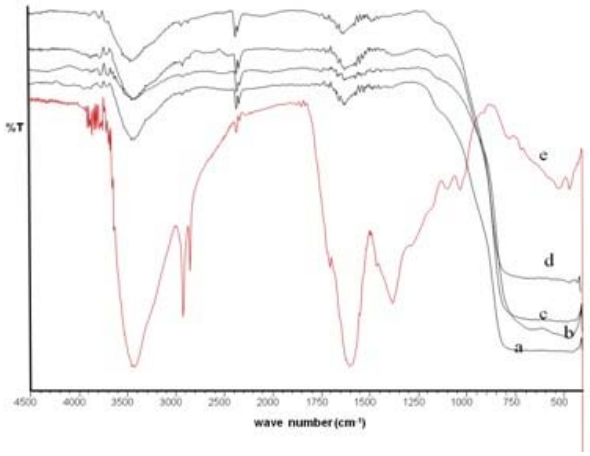

Figure-6. FTIR spectra of TiO_2 photocatalyst and humic acid. a) TiO_2,b) TiO_2 thin layer, c) TiO_2 thin layer absorbed by humic acid,d) TiO_2 thin layer after humic acid photocatalytic reaction,e) humic acid.

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.

4. CONCLUSIONS

The anatase TiO_2 has been successfully coated onto the surface of glass by screen printing techniques. The characterization results given an information that the resulting film is really crystalline and mesoporous TiO_2. The Surface layer is quite smooth with an average loading catalyst found to be 0.053 g/cm^2 andcoating thickness around 0.175 µm. A thin layer TiO_2 has proven worthy applied as a TiO_2thin layer photocatalytic solar reactor to degrade humic acids contents in the peat water for a relatively long duration. Photocatalytic reaction for six hours makes peat water be colorless, TOC decreased in water to94% and the water became neutral. The results of this research become potential and strategic solutions to transform peat water into a new source of clean water.

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