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Preparation of bifunctional ceramic membrane based on TiO_2/Kaolinite for Water Desinfection

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Abstract

This research was aimed to prepare bifunctional ceramic membrane for drinking water preservation especially in photocatalytic bacteria desinfection. Ceramic membrane was prepared based on TiO_2/kaolinite composite. First step of the investigation was synthesis and characterization of TiO_2/Kaolinite at varied Ti content followed by examination of its photocatalytic desinfection activity. Study on the effect of flow rate in the photocatalytic filtration by using formed ceramic membrane was also discussed.

Keywords: TiO_2, Photocatalysis, Desinfection, Ceramic Membrane

Introduction

Clean water becomes important thing in our daily life. One of these water demand is clean and drinking water in that more about 10,000-12,000 kilometers of fresh water required worldwide annually. In order to preserve a healthy and safe water In present work, some investigations reported many technologies applicable for community such as reverse osmosis process, adsorption, ozonitation and chemical treatment of soil water to drinking water [1]. Reverse osmosis using ceramic membrane filtration process is the most popular process due to its cheap and easy to be applied [2]. The effectivity of the process depend on the character and filtration efficiency of membrane material. The character such a high porosity and high adsorption capacity are the requirements for removal undesirable impurities fom water by the principle of adsorption. The improvement of bifunctional ceramic membrane should be cultivated to extent the lifetime performance of the filtration process, for example by combining photocatalytic and adsorption process simulaneously. Basic principle of photocatalytic treatment is generating radicals from the interaction between light and a photocatalyst [3,4]. Sufficient energy of photon stimulates electrone transition leaps from valence band to conductance band and left electrone hole in valence band. The interaction between holes and solvent releases some radicals. The generated radicals can furthermore oxidize bacteria, and also accelerate the removal of organic content in water. Some semiconductor metal oxides are photocatalyst and its composite form are reported. Among these, titanium dioxide is a widely used as photocatalyst in environmental applications refer to its effectivity and non toxicity. The combination of TiO_2 and porous silica alumina are reported to be more economist material in the term of combined photocatalysis and adsorption [5–8]. Based on these background, the preparation of bifunctional ceramic membrane from composite of TiO_2 and silica alumina material is interesting topic. While kaolinite is cheapest material for producing ceramic membrane, a bifunctional ceramic membrane can be developed from the composite of TiO_2 and kaolinite[9]. Aim of this project is to prepare bifunctional ceramic membrane by using TiO_2/Kaolinite composite for drinking water preservation. Effect of important parameter in TiO_2/Kaolinite preparation; TiO_2 content is studied by some material analysis such as XRD measurement, specific surface area and band gap energy analysis. For photocatalytic evaluation, the ability of prepared TiO_2/Kaolinite and its ceramic membrane form to reduce *E.coli* bacteria was calculated.

Materials and Method

2.1. Materials

Clay: raw kaolinite clay was obtained from Sukabumi, West Java, Indonesia. The raw material was dried at 80 °C before was grounded in a ball mill and passed through 200 mesh screen. Some chemicals were used as purchased consist of titanium isopropoxide(Sigma-Aldrich), isopropanol(Merck-Millipore) and ammonium nitrate.

2.2. Methods

Preparation and Characterization of TiO_2/Kaolinite : TiO_2/Kaolinite designed as Ti/Kao was prepared by using titanium isopropoxide as titanium(TTIP) precursor with impregnation method. Solution of TTIP in isopropanol solvent was dispersed into kaolinite dispersed in isopropanol:water solvent with varied theoretic content of Ti : 5; 10; and 20 %wt. The mixtures were stirred for 24h before were dried and calcined at 500^{o}C.

Characterization Techniques

Physicochemical characterization to the obtained materials was conducted by using x-ray diffraction(XRD) measurement, N2 gas adsorption-desorption analysis, scanning electrone microscope-Energy Disperssive X-ray(SEM-EDX) and Diffuse Reflectance UV-Visible (DRUV-Vis) spectrophotometri. X-ray diffraction (XRD) patterns of powder samples,using 2h ranging between 2^o and 80^o at a scanning rate of 4^o/min were obtained at 40 kV and 30 mA on a Philips diffractometer with Ni-filtered Cu Kα radiation. For SEM-EDX analysis was conducted using a instrument and for BET surface area and porosity analysis, NOVA 1200 instrument was utilized. Thermal analysis was performed on the Perkin–Elmer analyzers TGA7 and DTA7 and all measurement was carried out at a heating rate of 10^{o}C/min ranging from room temperature until 700^{o}C under a flow of air. Diffuse Reflectance–UltraViolet Visible (DR–UV–Vis) spectroscopy studies were recorded in a Shimadzu spectrometer UV-2100.

Preparation of Ceramic Membrane: Ceramic membrane was prepared by mix TiO_2/Kao with ball clay and dried saw dust in a certain proportion. The mixture was aged before pressed to obtained round form.

Photocatalytic Test: Photocatalytic Test of Ti/Kao samples for water desinfection experiments were carried out in the batch reactor consist of a water jacketed beaker glass under UV light expossion with 20cm distance. For each test, prepared Ti/Kao was dispersed into water and irradiated for 10mins. Total amount of *E.coli* bacteria before and after treatment was counted by most probable number methode. For ceramic membrane samples, a flow system of water desinfection was employed. Schematic representation of both photocatalytic system is presented in Figure 1.

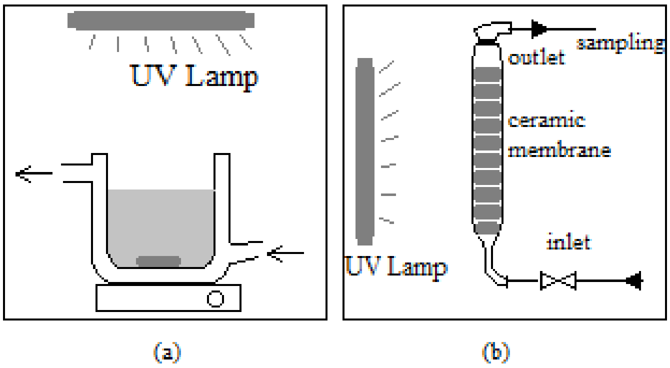

Figure 1: Scheme of batch system photocatalytic test of Ti/Kaolinite(a) flow system photocatalytuc test of ceramic membrane(b)

Result and Discussion

3.1. Characterization of TiO_2/Kaolinite

The XRD spectra in Figure 2 indicate there is a progressive decrease in intensity of kaolinite specific reflections after TiO2 immobilization at all varied concentrations. Characteristics reflections of kaolinite are shown at 2θ= 20.0^o (d=4.34); 24.9^o(d=3.57); 34^o(d=2.56); 60^o(1.54) and 62^o(d=1.49) and other reflections as indication of quartz as impurities . After was modifief with TiO_2, the dominant reflections were from the indication of titanium dioxide in anatase phase and rutile phase[10]. From varied titanium content, the difference is not significatly appeared and assuming that the formation of titanium particles on surface was observed. This hypothesis is relevant with surface profile of materials from SEM analysis in Figure 3.

Figure 3 expresses the morphological changes of TiO2/K along with increasing TiO_2 content as can be seen from appearance of the surface. Effect of TiO_2 addition on the formation of a composite with a porous structure identified by the presence of some form of granules on surfaces which are indication of dispersed titania particles. The formation of aggregates on surface is in line with adsorption-desorption profiles (Figure 4) and calculated surface parameter of specific surface area, pore volume and pore radius data are listed in Table 1.

The obtained data from Figure 4 and Table 1 suggest that there is a relationship between TiO_2 content in Ti/Kao composite with the changes in specific surface area, where the greater the concentration of TiO_2, the greater the specific surface area. Large concentration of lead particles can cover the pores so that the total pore volume of the irregularities. For example the total pore volume of the Ti/Kao-10 is lower than the Ti/Kao-5and Ti/Kao-20. The most probable reason for this is that at Ti/Kao-20 the titania particles is too much and creates their own cavity, thus forming new pores.

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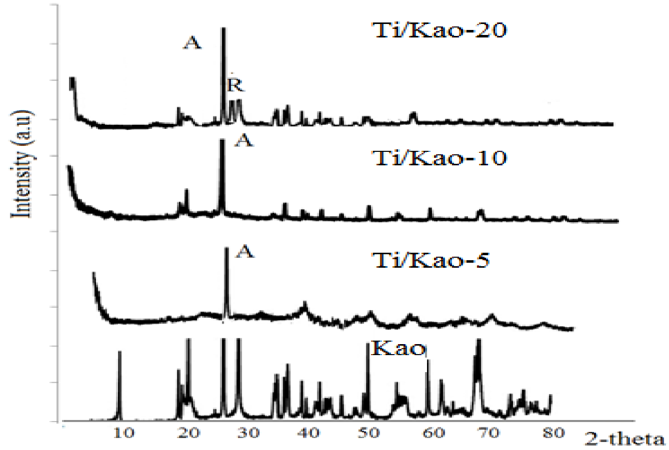
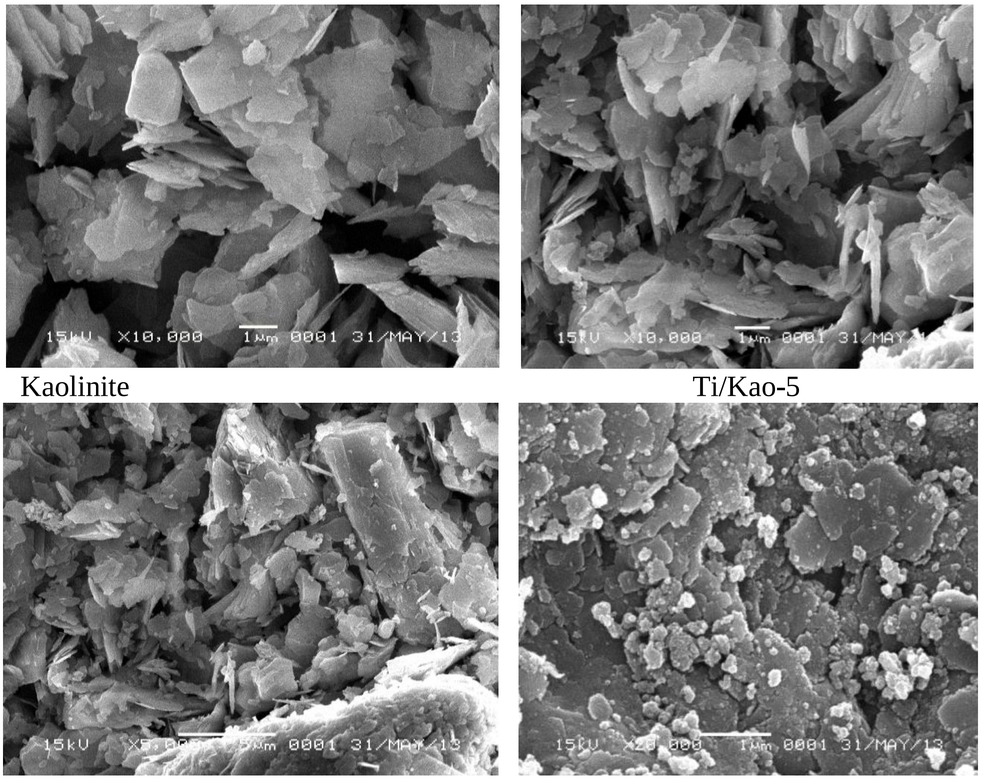


Figure 2: XRD Pattern of Ti/Kao compared with raw kaolinite



Kaolinite Ti/Kao-5

Ti/Kao-10 Ti/Kao- 20

Figure 3: SEM Profile of Ti/Kao samples and Kaolinite.

Table 1. Data hasil analisis BET Ti-Kao 5%, 10%, 20% dan Kaolin

Material	**Specific Surface Area (m^2/g)**	**Total Pore Volume (x10 $^{-1}$cc/g)**	**Pore Radius (10 ^{2}Å)**
Kaolin	7,659	2,846	1.49
Ti/Kao-5	22.105	1.017	1.84
Ti/Kao-10	28.378	6.578	1.86
Ti/Kao-20	40.928	1.216	1.19

DRUV-Visible spectrophotometry spectra was observed to identify effect of Ti conten on band gap energy value. The spectra in Figure 5. exhibits that edge wavelength of Ti/Kao samples are in following order : Ti/Kao-10< Ti/Kao-20< Ti/Kao-5 corresponding to band gap energy value at reverse order so that Ti/Kao-10 has the highest value. The calculated band gap energy of Ti/Kao-10 is 3.21eV slightly higher compared to band gap energy of anatase. The lower band gap energy of other Ti/Kao samples is related to the chrystallinity of anatase and the presence of rutile in Ti/Kao-20.

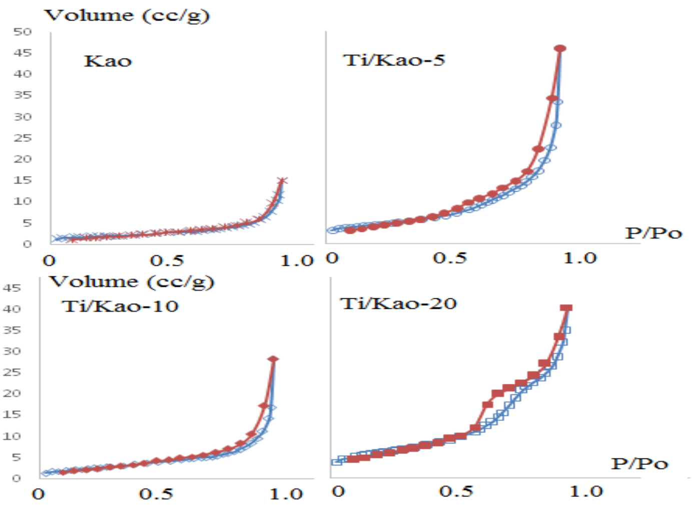


Figure 4: Adsorption-Desorption Profile of Materials

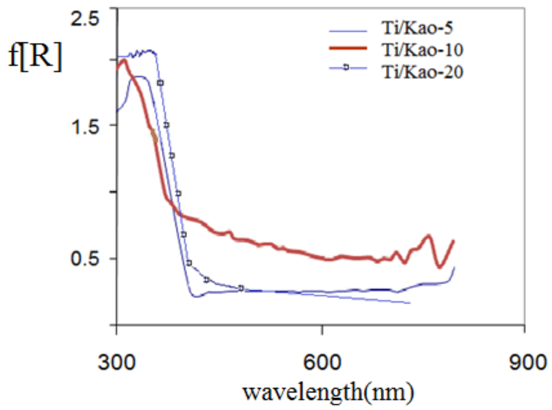


Figure 5: DRUV-Vis spectra of Ti/Kao samples

3.2. Photocatalytic Test

Principles of photocatalytic bacterial desinfection is that the presence of photocatalyst in combination with UV light is able to inhibit the growth of bacteria. Photocatalytic disinfection method is not only able to kill bacterial cells and tissue damage, but also able to degrade toxic compounds released by cells that have died. The succeed of this method depends on the photocatalyst used.

The mechanism of photocatalytic desinfection is proposed to be similar with the desinfection over pure TiO_2. The interaction between light and photocatalyst will generates electrons from the valence band will be excited into the conduction band, forming electron–hole (e^- - h^+) pairs in the TiO_2 nanoparticle. These charge carriers may either recombine or react with electron donors and acceptors adsorbed onto the TiO_2 surface. Positive holes in the valence band interact with water molecules to generate extremely reactive hydroxyl radicals which will then inactivate pathogens during the process of photocatalytic water disinfection [11]. Photocatalytic activity is affected by the adsorption capability, the particle size and other physicochemical parameters.

Photocatalytic test of Ti/Kao samples is showed by the percentage of total bacteria after each photocatalytic treatment by following equation:

$$\text{Photocatalytic desinfection activity(\%)} = \frac{(initial\ \ bacteria\ \ level - after\ \ treatment\ \ bacteria\ \ level}{initial\ \ bacteria\ \ level} x100$$

The comparison on photocatalytic desinfection activity is presented in Figure 6. In general, the photocatalytic desinfection of TiO_2/Kaolinite composites are not significantly different with that of pure TiO_2. It means that the titania dispersion on kaolinite as supporting material ranging from 5-20% gives similar activity compared to pure one while raw the desinfection activity by using raw kaolinite gives the lowest value so the composite form gives advantageous as more economical material. The raw kaolinite reduce total bacteria by only adsorption mechanism and does not conduct photocatalysis mechanism. From the variation of Ti content, it can be seen that Ti/Kao-10 gives highest desinfection activity while Ti/Kao-20 is the lowest. This desinfection activity seems to be related to the band gap energy and also the presence of anatase phase in Ti/Kao-10. Even the titania content of Ti/Kao-20 is the greatest but the presence of rutile phase as detected from XRD profile is probably affect to the photocatalytic activity.

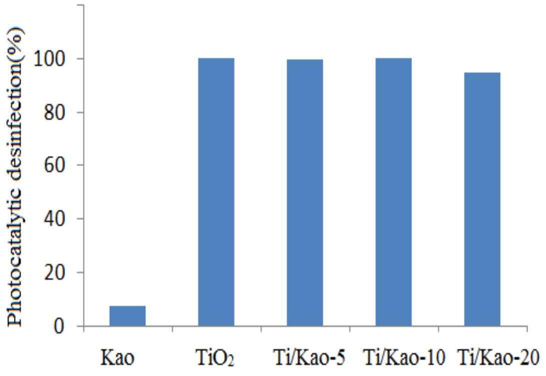


Figure 6: Photocatalytic desinfection activity of kaolinite and prepared Ti/Kao samples

Furthermore, effect of Ti/Kao dosage to the photoactivity in the desinfection system was studied by varying composite weight 0.05g/L ; 0.15g/L and 0.3g/L. Profile of the effect of Ti/Kao dosage to the photocatalytic desinfection activity is presented by Figure 7. From varied dosage it can be noted that in the best desinfection was obtained by Ti/Kao-20 at the dosage of 0.15g/L. For both Ti/Kao-10 and Ti/Kao-20 it is seen that the higher the dosage the desinfection increases while for Ti/Kao-5 the optimum condition is at the dosage of 0.15g/L. The lower desinfection at 0.3g/L is probably caused by the incresing turbidity of solution that prevent the entrance of UV light into the system. This is similar with the trends in photocatalytic degradation over some immobilized TiO_2 [12]

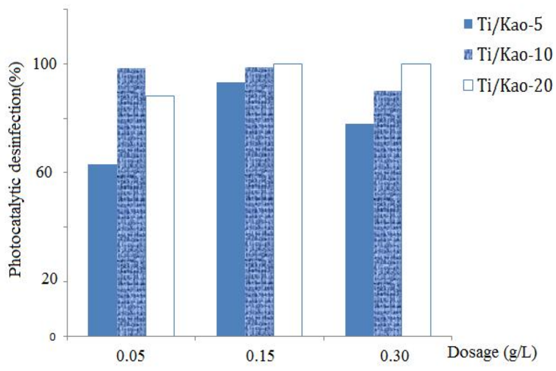


Figure 7: Effect of Ti/Kao dosage to the photocatalytic desinfection activity

3.3. Photocatalytic Test of Ceramic Membrane

Refer to photocatalytic data of of Ti/Kao, preparation of ceramic membrane was performed by adopting optimum condition. Ceramic membrane filter was prepared by using Ti/Kao-20 in composition with other ingredients such as ball clay, $CaCO_3$ and sawdust as porous forming in calcination step at 950^{o}C for 6h. From flow system of photocatalytic desinfection test at two varied flow rate of 100mL/h and 500mL/h, changes in bacteria level along sampling time is demonstrated by Figure 8.

The treatment with UV light means that the process was photocatalytic desinfection gives the higher desinfection compared to as with out UV light which mean only the adsorption mechanism. The higher photocatalytic desinfection along varied sampling time is obtained at lower flow rate (100mL/h) is attributed to the more intensive interaction between ceramic membrane and bacteria in water sample. At the begining, the desinfection activity is very high (almost 100%) and then simultaneously decreased and then being constant along the sampling time of 5-10h. In contrast, from the flow rate of 500mL/h the desinfection is relatively constant. The higher photocatalytic desinfection value indicates that low flow rate is required to produce standard acceptable drinking water eventhough at general ceramic membrane showed the bifunctional properties.

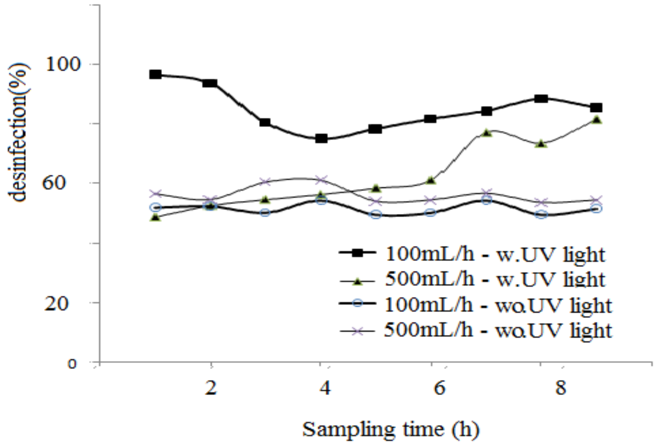


Figure 8: Desinfection activity of ceramic membrane

Conclusion

Ceramic membrane has been succesfully prepared based on TiO_2/kaolinite composite. TiO_2/Kao is a promising composite photocatalyst material in ceramic membrane filtration as shown by the percentage of desinfection activity againts *Eschericia coli* in water. The combination of filtration and photocatalytic oxidation can produce synergistic effects influenced by TiO_2 content in the composite and also flow rate in the filtration system.

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