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Synthesis of TiO_2/Chitosan Photocatalyst, TiO_2/Bentonite and Adsorption of Zeolite to Purify Unnes's Water Reservoir

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Abstract: The condition of water reservoir is alarming now because it looks more cloudy and dirty. Water had contaminated not only organic trashes, but also inorganic. So it can not be used for rainwater catchment as the first function by residents and the surrounding area as well UNNES to recreation .The purpose of this study is to provide solutions in an attempt restoration of water reservoir with purification process based on TiO_2/chitosan photocatalysts, TiO_2/bentonite when exposed to visible light will generate OH radical compounds that function as degrading organic pollutants and compounds superoxide. In addition to the photocatalyst, the study also did zeolite adsorption. Based on the results of SEM (Scanning Electron Microscopy) above it can be concluded that: In the SEM magnification 100X, 250X, 500x, and 1000x seen that the coated material has not been good and still lumpy and uneven. The result of the formation is characterized by using X-Ray Diffraction, Fourier Transform Infrared (FTIR). TiO_2-bentonite composite formation has not changed is still the same at wave number. Based on the results of BOD and COD was found that with the technology photocatalyst TiO_2 /chitosan, TiO_2/ bentonite and zeolite adsorption can degrade organic pollutants in the water and can reduce BOD and COD in Air embung UNNES.
Key Words : Air Embung, TiO_2/chitosan, TiO_2/bentonite, zeolite adsorption.

Introduction

Water conservation is one thing that is very supportive Semarang State University as a green campus which is characterized by many trees in its surrounding. Water conservation in the principle is the use of rainwater that falls onto the land surface efficiently with the right time setting of water flow so there is no flooding in the rainy season and there is enough water in the dry season[1]. Water conservation can be done by increasing the utilization of hydrological components such as surface water and groundwater as well as improving the efficiency of irrigation water use[2]. Water conservation technologies designed to improve the ingress of water into the soil through an infiltration process and filling the water pockets in the basin as well as reducing water loss through evapotranspiration and it evaporates into the atmosphere[3]. One strategy to achieve water conservation and also an effective way that can be done to increase the capacity of groundwater reserves is the manufacture of water reservoir. Embung is essentially a small dam measuring 75 x 500 m or smaller about 20 x 40 m with a depth from the soil surface or weir crow about 1.5 – 6 m high. Embung has a function as a rainwater and runoff, as well as to ensure the availability of water at the end of the rainy season until the end of the dry season.

Embung Unnes located next to the building of the Faculty of Language and Art. In essence the manufacture of reservoirs intended to be used as a water reservoir during the rainy season and as a source of water during the dry season for people lived around campus. In addition, the presence of reservoir has created a new ecosystem that is a lively place for fish in it, creating a green space as a park for studying, gathering and carrying out positive activities like discussion, and others. However, over time, reality has shown that the water reservoir had changed either environmental quality or functionality. Currently the stored water in Unnes's reservoir is very murky, smelly, and green. In order for optimal function of water reservoir needed an attempt to overcome this problem is by photocatalysts and adsorption systems.

Wastewater treatment technologies can be done with photocatalyst process. Photocatalyst is a chemical reaction that runs with the aid of a catalyst and this catalyst will active when exposed to sunlight. This technology is one method that is used for wastewater treatment. This process can also be called a continuous oxidation process that is suitable to oxidize the dye. Continuous oxidation process is based on the formation of hydroxyl radicals (OH•) which is a strong oxidizing agent that can promote total mineralization on persistent organic pollutants[4,5,6,7,8].

TiO_2 catalyst must be activated using energy photon with small wavelength. Photocatalyst material that had become the focus of many scientists research in the world is Titanium Dioxide (TiO_2). TiO_2 is a dioxide compound that has white color which is rust resistant and non-toxic. Beside that titanium dioxide is one of the most stable catalysts, and most commonly used in the comparison with other catalysts[9,10,11,12,13]. Semiconductor photocatalyst using TiO_2 as a photocatalyst has been done to solve various environmental problems, such as, for the purification of water and air, destruction of microorganisms like bacteria and viruses in the activation of cancer cells, the degradation of dyes, toxic chemical compounds and the manufacture of hydrogen gas from water [14].

From some advantages of TiO_2 photocatalytic method, it still has some weaknesses in degrading the waste, such as: first, the lack of adsorption ability so the contact between TiO_2 with waste in the photodegradation process was not optimal. Second, the turbid state, UV rays will be blocked by particles of waste that can not activate the TiO_2 photocatalyst material, with the conventional techniques, it is relatively difficult for the TiO_2 photocatalyst taken up again [15].

To cover up these weaknesses, the developing of photodegradation process by TiO_2 started with adding the carrier material which has a good adsorption capabilities. Carriers used in this study is chitosan and bentonite. Chitosan is regarded as an excellent carrier material because it can eliminate a variety of organic and inorganic waste. Beside that, chitosan also has some advantages such as non-toxic, antibacterial, biodegradable and abundant existence as a crustacean shell waste, so that chitosan is very potential to be developed[16]. While bentonite is one type of clay which has (85% -95%) mineral montmorillonite as the main ingredients with a general chemical formula $Mx(AL_4\text{-}xMgx)Si_8O_{20}(OH)_4$ n H_2O. Bentonite has the ability to swell (swelling), has exchangeable cations, and can be intercalated[17].

In addition to using the principle of photocatalyst, the research also uses the principle of adsorption by gravel and zeolites. Zeolite is one alternative adsorbent that has high adsorption capability. Because It has many pores, high cation exchange capacity and can be applied at a wide temperature range, so it is very suitable to be used as an adsorbent[18]. Zeolites have been widely used as an adsorbent because of its ability to separate the target species through ion exchange principle[19]. In this experiment used of natural zeolite powder. Zeolite powder is used for activating the zeolite physically by the grain size reduction and sieving to remove from organic impurities, pores enlarge and expand the surface area of zeolite[20]. Use of zeolite powder Because It has characteristic Including dehydration, adsorbents and molecular sieves, catalysts, and ion exchange. Among These characteristics, the adsorbent and filter molecules are the basic use of zeolite. Adsorption is a surface phenomenon, this is the addition of the concentration of certain components on the surface between the two phases [21].

Previous research has been done by Nugroho (2011)[22], namely organic waste water processing system based photocatalyst material titania (TiO_2) that is used to treat organic wastewater. TiO_2 photocatalytic reactions has proven to clear up, eliminate odors, reduce the TDS value about 44.08%, BOD is about 73.44% and COD is about 71.21% in organic wastewater. In addition, research conducted by Wibowo (2016) [23]based on TiO_2/chitosan proven that it can degrade organic pollutants in water and can reduce BOD and COD.

Based on these background, this study aimed to compare the effectiveness among the using of TiO_2/chitosan, TiO_2/bentonite as photocatalyst material, and adsorption process using zeolite and gravel to decrease BOD and COD Unnes's water reservoir.

Experimental

Material and Equipment

Materials used in this study is water reservoir 600 ml, 1 M NaOH, 1% acetic acid (*v*/*v*), TiO_2, bentonite, chitosan, gravel, and zeolite. Tools used in this study include beaker glass, stir bar, pH indicators, funnel, X-Ray Diffraction (XRD) Shimadzu, Scanning Electron Microscopy (SEM), FTIR Shimadzu, 3 pieces of PVC pipe measuring 16 cm in diameter 8 cm, 2 pieces of fabric with the measurement of 10 cm x 10 cm, a set of test parameters Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)

Synthesis of composite TiO_2-bentonite

Five grams of purified montmorillonite was dispersed in 500 ml of distilled water and stirred for 5 hours until the lumps of clay was lost. 2.5 grams of TiO_2 dispersed in 100 ml of distilled water and then stirred and added to the mixture of bentonite. TiO_2-bentonite mixture then roasted at 100°C for 2 hours [24]. The resulting composite was then characterized using XRD, SEM and FTIR.

Synthesis of TiO_2-Chitosan

First the TiO_2 dissolves in 100 ml of acetic acid 1%, ± 2 hours stirring continuously at a constant speed. After that added 0.4 grams of chitosan, and stirring quickly ± 2 hours continuously to obtain clear sol. Then added 1 M NaOH solution into these sol dropwise until solution reaches pH = 10. Then put in oven at 100°C for 4 hours and calcined at 450°C for 2 hours TiO_2-chitosan material is ready to use[23].

Photodegradation of water reservoir using a composite TiO_2/bentonite and TiO_2/chitosan

Photodegradation was done by dispersing 0.3 grams of TiO_2, bentonite, and TiO_2-bentonite and TiO_2/chitosan into 300 ml of water reservoir followed by stirring for 30 minutes. Time parameter for 30 minutes is the optimum time based on the research of Wibowo*et al.*, 2016[23].

Adsorption of air embungUnnes with Pebble and Zeolite

The method used in this experiment is combintion of many tools into a series so it will form a pipe with two layers of filters with a fabric each of layer. On the top layer by gravel and the lower by the zeolite powder. Air embungUnnes 1.5 liter filtered through both of layers. After that, testing the number of BOD and COD in the water that has been filtered. This test was done in BBTPPI Semarang.

Results and Discussion

Characterization

The results of the analysis of Fourier Transform Infrared (FTIR)

The results of spectroscopic analysis of TiO_2 powder, bentonite, and TiO_2-bentonite presented in Figure 1. Ti-O between the range 400-700 cm^{-1} in this case is shown in peak 478.35 and 594.08 [25]. The main absorptions peak on bentonite is located at wavenumber 3626.17 cm^{-1}, 3448.72 cm^{-1} and 1635.64 cm^{-1}. At the peak of 3626.17 cm^{-1} shows the stretching vibration of O-H located in the octahedral layers bonded to Al whereas the absorption peak at 3626.17 cm^{-1} shows the vibration H-O-H molecules of water in the interlayer structure of bentonite. In addition, the absorption peaks around 3448.72 cm^{-1} shows the vibration of O-H corresponding to the absorption peak at 1635.64 cm^{-1}

TiO_2-bentonite spectra did not indicate any shift in absorption at wavenumber 3448.72 cm^{-1} which is not shown O-H bond is weakened by the existence of TiO_2 in between layers of bentonite. Wavenumber 3448.72 cm^{-1} is an O-H stretching vibration of H_2O trapped in between the layers of bentonite. Another possibility for the influence of calcination and heating so that the group O-H from H_2O many hydroxylated and dehydrated from the interlayer.

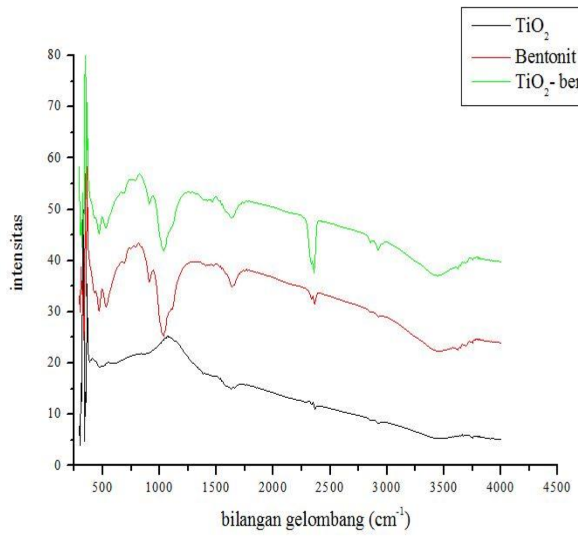
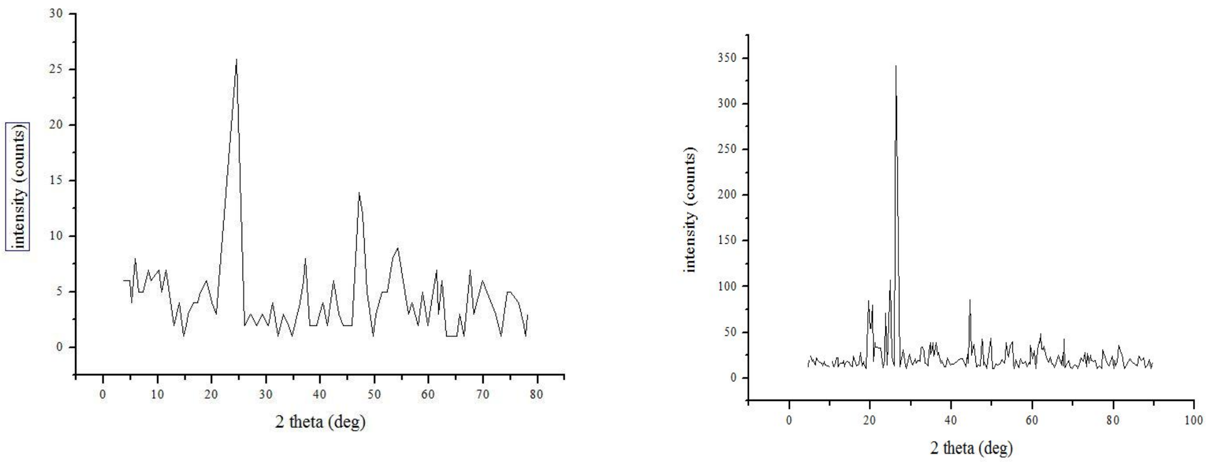


Figure 1. The spectra of TiO_2, bentonite and TiO_2/bentonite

The results of the analysis of X-Ray Diffraction (XRD)



(a) **(b)**

Figure 2. Test crystallinity (a) TiO_2 and (b) TiO_2–bentonit using XRD

Difaktogram reflection pattern on TiO_2 composite shown in 2θ of 25.31; 38.58; 48.34; 53.91; 62.72 which is characteristic diffraction from crystal planes 101, 004, 200, 105 and 204 TiO_2 anatase (A) in accordance with JCPDS No.21-1272 (Saraswati and Nugraha, 2014). The peaks of the TiO_2 reflections also appear on difaktogram composite TiO_2/bentonite namely at 2θ of 26, in 2608; 36.7121; 47.4609; 53.5; 62.02. Reflections on the 2θ shows the crystal phase contained in the composite TiO_2-bentonite is anatas crystal phase. These results indicate that the formation of composite TiO_2-bentonite does not alter the crystallinity of TiO_2 significantly, it means that is not significantly reduce the photocatalitic activity.

Analysis Scanning Electron Microscopy (SEM) and EDX

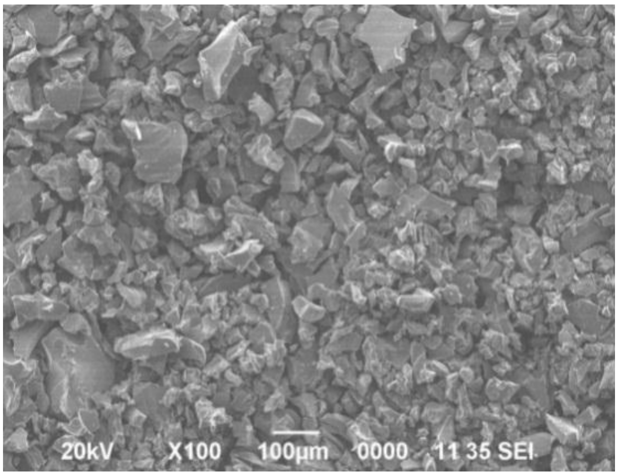


Figure 3. Morphology of TiO_2 SEM magnification of 100 x

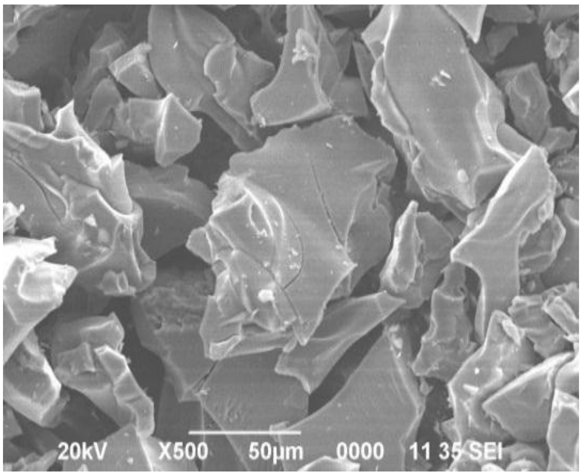


Figure 4. SEM morphology of TiO_2 magnification 1000 x

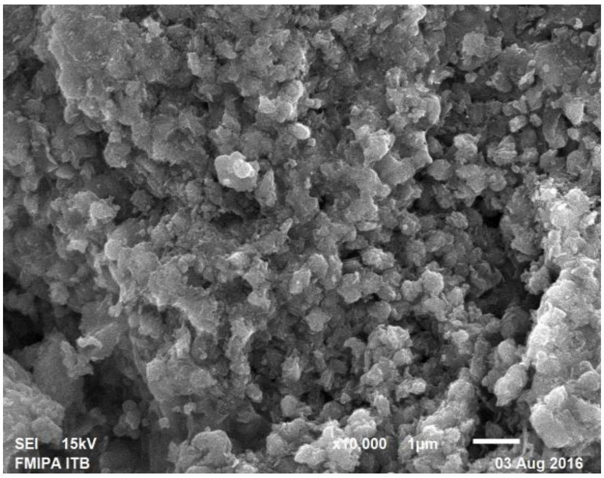


Fig 5. SEM morphology TiO2-bentonite Magnification 10,000 x

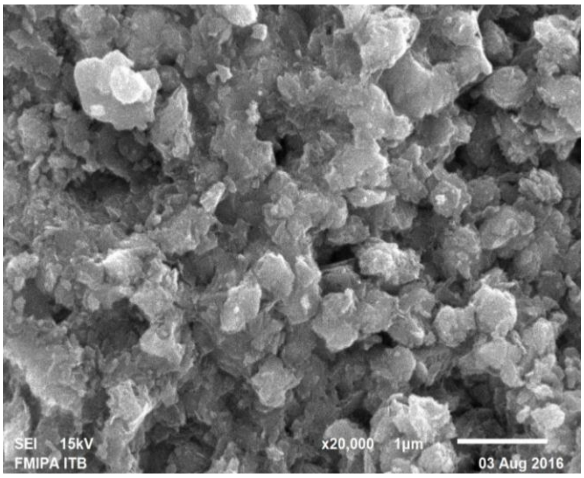


Fig 6. SEM morphology TiO2-bentonite Magnification 20,000 x

Based on the results of SEM (Scanning Electron Microscopy) above, it can be concluded that: In Figures 3 and 4, SEM magnification of 100x and 1000x seen that the coated material has not been good and still lumpy and uneven. This is because less mixing of old and aging time were only briefly that will affect the morphological structure of TiO_2 produced. Based on the results of SEM (Scanning Electron Microscopy) conducted in FMIPA ITB in Figure 5 and 6, it can be concluded that: In the SEM magnification 10.000 x and 20.000x seen that the coated material has not been good and still lumpy and uneven. This is because less mixing of old and aging time were only briefly that will affect the morphology of TiO_2/bentonite produce.

Based on the results of the EDX can be seen that in the womb composite TiO_2/bentonite are O component of 49.41%, Al 4.47%, amounting to 5.69% Si, Ti of 1.84% and amounted to 38.60% Fe.

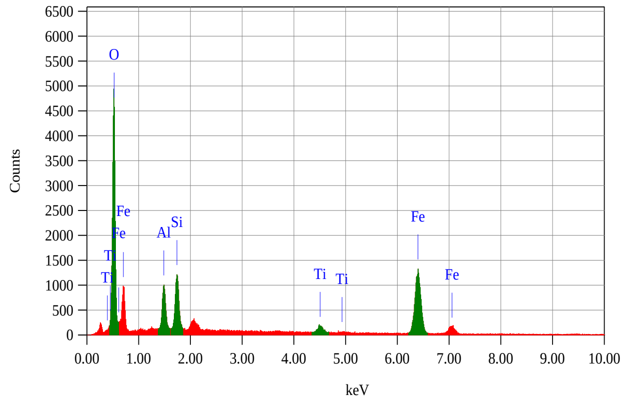


Figure 5. The results of the analysis with EDX

Photodegradation Embung with TiO_2, bentonite, and composite TiO_2/bentonite.

Table 1. Test BOD and COD

No	Sample	Parameter	Result (ppm)
1	Air embung with bentonite	BOD COD	54,84 20,24
2	Air embung with TiO_2.bentonite	BOD COD	18,40 10,05
3	Air embung with TiO_2-chitosan (10 minute)	BOD COD	54,33 42.29
4	Air embung with TiO_2-chitosan (20 minute)	BOD COD	41.73 18.07
5	Air embung with TiO_2-chitosan (30 minute)	BOD COD	39.37 16.55
6	Zeolite	BOD COD	28.96 37.15

This study aims to provide a comparative picture between the activity of TiO_2/chitosan, TiO_2/bentonite and adsorption using zeolite and gravel of water reservoir. The biggest impairment of BOD and COD obtained by using TiO_2-bentonite about 18.40 ppm of BOD and 10.05 ppm of COD. TiO_2-bentonite composite capability greater than TiO_2 catalyst and bentonite. This is caused by the presence of TiO_2 photocatalyst contained in the composite TiO_2-bentonite. When exposed to radiation of visible light, the electrons in the valence band of the semiconductor be excited into the conduction band which will generate e- and emptiness or hole (h^+). The next hole (h^+) reacts with hydroxide titan contained in solution to form titan hydroxide radicals which will oxidize water reservoir. This Radicals hydroxide will be formed continuously as long as the visible light (lamp) still contact with the composite and will attack the water reservoir so that the water reservoir will be degraded in this case the BOD and COD.

Conclussion

Based on the research that has been done, it can be concluded that the synthesis of TiO_2-bentonite composites are found physical interaction and the biggest decreasing of BOD and COD level obtained using TiO_2-bentonite about 18.40 ppm BOD and 10.05 ppm of COD. TiO_2-bentonite composite capability is greater than TiO_2 catalyst and bentonite.

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