



## Decoloration and microorganism degradation from biodeinking waste using flow system of photoelectrodegradation

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### ABSTRACT

Degradation process results fotoelektrokatalitik from waste of biodeinking with photoanoda Ti / TiO<sub>2</sub>-NiO with flow system had been achieved. This research aims to study the activity of photoanoda TiO<sub>2</sub> / NiO on waste photoelectrocatalitic degradation of dyes and the number of microorganisms biodeinking. Preparation photoanoda Ti / TiO<sub>2</sub>-NiO done with the technique of wet impregnation, then composite TiO<sub>2</sub>-NiO sprayed on the surface of the electrode Titanium. Photoanoda characterization is done by X-Ray Diffraction (XRD), fourrier Transform Infra Red (FTIR) and TEM-SEM .. XRD diffractogram TiO<sub>2</sub>-NiO composite showed characteristic peak of TiO<sub>2</sub>-NiO at 2θ = 33°. NiO existence characterized by FTIR absorption Ni-O at 412.77 cm<sup>-1</sup>. Meanwhile, TEM and SEM analysis showed TiO<sub>2</sub> with crystal size in the region of 50 nm on the surface of Ti plate. Fotoelektokatalitik degradation dye waste results biodeinking done using photoanoda Ti / TiO<sub>2</sub>-NiO and Ti cathode using a halogen lamp 300 W / m<sup>2</sup>. Results of the maximum degradation of dye wastewater biodeinking results shown in the voltage 6 volts with a flow rate of 3 mL / sec with% 90.10% decolorination reached. While the number of bacteria content analysis was performed using the method PJB (Calculation of Total Bacteria) with optimum results on the bacterial degradation of voltage 6 volts.

**Keywords:** bacteri, dye, photoelectrodegradation, waste of biodeinking

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### INTRODUCTION

Reduced availability of raw materials pulp and paper industry are derived from natural sources of fiber (virgin pulp) and the proliferation of global warming due to forest loss as the lungs of the world, has been pushing the pulp and paper industry to look for sources of raw materials of non-timber or better known as secondary fiber. Secondary fiber has become a very important raw material for pulp and paper industry. In addition because the price is cheaper, can also help to preserve forests, reduce environmental pollution and reduce the use of water and energy. One source of paper that can be used as a source of secondary fiber is used newspapers. This is because newsprint is one type of paper that is widely used as the print media are published daily in large quantities and after being read normally be disposed. This old newspapers must undergo removal of various contaminants before undergoing the process of papermaking, one of the contaminants are difficult to remove the ink. Deinking process is usually through conventional deinking process.

The deinking process is a process that produces solid waste that is classified as B3 waste from specific sources (Government Regulation No18 / 1999 and 85/1999 on Management of Hazardous and Toxic). In general, the solid waste containing toxic heavy metals derived from the water-soluble ink waste [6]. However, with developments in the field of biotechnology, conventional deinking process used for the processing of old newspapers began to turn with biodeinking process uses an enzyme to remove contaminants ink from old newspapers [9].

Biodeinking is a waste newspaper deinking process uses enzymes to replace chemicals in conventional deinking process. Enzymes that have been carried out research for the biodeinking process as xylanase enzyme derived from *Bacillus subtilis* PC-01 and cellulase derived from *Bacillus stearothermophilus* [12]. With the use of these enzymes, biodeinking process will reduce the amount of usage of chemicals of conventional deinking process making it more environmentally friendly. However, the results biodeinking process still produces a B3 waste originating from the ink dissolved in the waste water of the biodeinking process. Besides that, there are other contamination from the biodeinking process is contamination of bacteria used in the biodeinking process. Therefore, prevention of waste dye ink and bacteria with a very practical and economical way need to be developed so that the paper industry is able to manage waste properly.

Some techniques or methods of waste reduction dyes have been developed, such as zeolite adsorption method as practiced [10]. However, this method is less effective because the dye adsorbed using zeolite can accumulate in the adsorbent feared that someday will lead to new problems. As an alternative solution, the need to develop a method by utilizing a catalyst diantaranya semiconductor photocatalytic degradation, degradation and degradation photoelectrocatalytic electrocatalytic based ultrafiltration to degrade the dye ink and the bacteria results biodeinking process.

Photoelectrocatalytic degradation is degradation reactions involving light (photons), catalyst and electrical flow together so as to improve the mobility of electrons excited in the photocatalyst [1]. External provision of the anodic potential on photoanoda couple  $\text{TiO}_2\text{-NiO}$  can reduce the recombination of electrons and holes and push the accumulated electrons excited by visible light so that the reaction  $\text{NiO}$  to  $\text{TiO}_2$  dye and bacterial degradation can occur as well as photooxidation fotoreduksi [5], In the system flow, photoelectrocatalytic degradation can also be influenced by the flow rate. The smaller the flow rate it is possible the process of degradation of dyes even greater because the contact frequency dye particles and bacteria with higher catalyst component. The greater the voltage applied would increase the current that can accelerate the flow of electrons and inhibiting recombination of electrons and holes.

Based on the above, this study focuses on the waste processing system with the result biodeinking photoelectrodegradation flow system. Sewage treatment system with photoelectrodegradation is expected to help eliminate particulate contamination dye ink once bacterial contamination from the waste biodeinking process effectively and efficiently.

## EXPERIMENTAL SECTION

### A. Biodeinking process

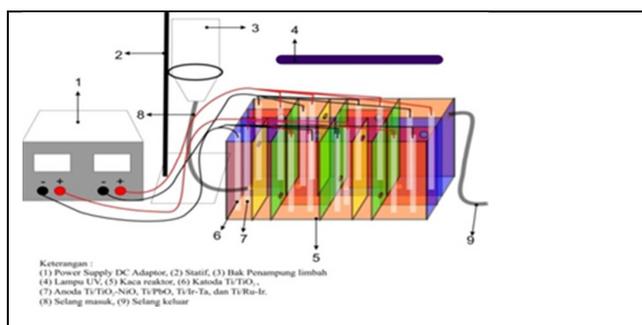
Old newspapers described in the beater with no load for 7.5 minutes, then the consistency of the stock 4%, pH 5 (with the addition of dilute  $\text{H}_2\text{SO}_4$  and  $40^\circ\text{C}$  added enzyme derived bacterium *Bacillus stearothermophilus* stirred for 30 seconds and allowed to react for 60 minutes to give chance enzyme degrades the fiber surface. After 60 minutes of added ice or cold water (temperature  $5\text{-}10^\circ\text{C}$ ) to stop the enzyme activity. Stock diluted to 0.8% consistency and heated to  $60^\circ\text{C}$ , then added the collector as much as 0.5% against the dry weight fiber. Then do the flotation process for 20 minutes. Stock outcome flotation washed until pH neutral. Then the bleaching process is carried out using NaOH 0.15% p no conditions pH 10 and  $70^\circ\text{C}$  for 60 minutes. Waste biodeinking process results are then separated for testing with photoelectrodegradation.

### B. Preparation electrode Ti / $\text{TiO}_2\text{-NiO}$

Preparation cathode thin layer Ti /  $\text{TiO}_2$  done by mixing 12.5 grams of  $\text{TiO}_2$  that has been mashed into 50 ml of ethanol. Then distirer and sonicated for 10 minutes to form a gel. Dispray gel formed on the electrode Ti and heated at  $200^\circ\text{C}$  for 10 minutes. Photoanoda Ti /  $\text{TiO}_2\text{-NiO}$  was prepared by mencampuran 12.5 grams of  $\text{TiO}_2\text{-NiO}$  which has been mashed into 50 ml of ethanol. Then distirer and sonicated for 10 minutes to form a gel. Dispray gel formed on the electrode Ti and heated at  $200^\circ\text{C}$  for 10 minutes to evaporate the ethanol.

### C. Preparation Glass Reactor

The reactor used as shown by Figure 1. Preparation of thin-layer Ti /  $\text{TiO}_2$  done by mixing 0.5 grams of  $\text{TiO}_2$  that has been mashed into 2.1 ml of ethanol. Then distirer and sonicated for 10 minutes to form a gel. Dispray gel formed in the glass reactor with a thickness of  $\pm 1$  mm and heated at  $200^\circ\text{C}$  for 10 minutes, to evaporate the ethanol.



**Figure 1. Photoelectrodegradation reactor**

#### D. Material Characterization

Characterization of TiO<sub>2</sub> results of the synthesis is done by using XRD and FTIR. Characterization of TiO<sub>2</sub>-NiO composite done using XRD, FTIR and TEM. And characterization of commercial electrode done using XRD.

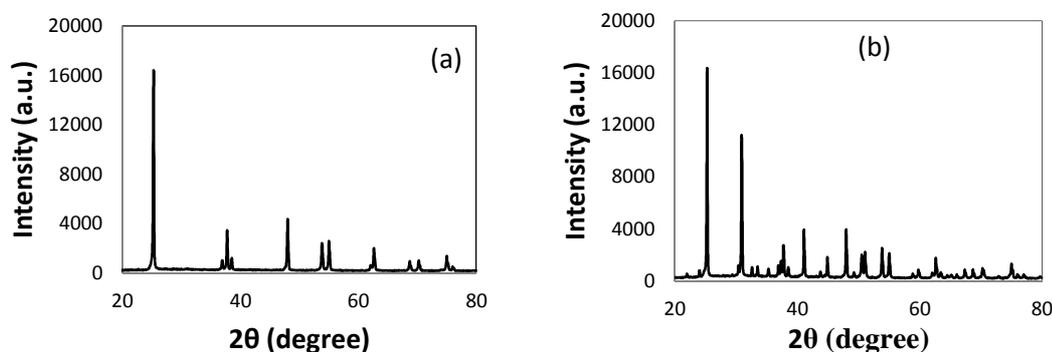
#### E. Measurement Process Degradation Fotoelektrokatalis

Photoelectrodegradation measurement experiments done by creating a flow reactor system can be bypassed by electrolyte NaCl. Where photocathode Ti / TiO<sub>2</sub> and photoanoda Ti / TiO<sub>2</sub>-NiO are in one reactor. Potentiostat used to set the bias voltage charged to the working electrode. 150 Watt halogen lamp used for visible radiation source.

Photoelectrodegradation measurement substrate (Waste Biodeinking) carried out by preparing the waste solution which results from the biodeinking process supplied with a flow rate of 3 mL / sec and 6 mL / sec in the reactor containing the working electrode and the counter electrode with a bias voltage variations (4; 5 and 6 Volt). Then analyzed by UV-Vis spectra to determine the change in absorbance of the dye after photoelectrocatalytic degradation and microbiological tests to determine the number of bacteria after relegation photoelectrocatalitic.

### RESULTS AND DISCUSSION

The first achievement of this research is the preparation photoanoda TiO<sub>2</sub>. Titanium dioxidewas prepared with technical TiO<sub>2</sub>. For photoanoda preparation, technical TiO<sub>2</sub> structure modification mechanochemical method by ball milling techniques. Report preparation and the characteristics of changes in the structure by this method are reported separately from this report. Changes that occur with this treatment is the inception phase of anatase and anatase phase decomposition brokrite large crystal size (Figure 1). To determine the presence of TiO<sub>2</sub> anatase phase, XRD analysis results are compared with the standard JCPDS (Joint Commite Powder Diffraction Standards). The diffraction pattern of TiO<sub>2</sub> synthesis results are shown in Figure 1. TiO<sub>2</sub> synthesized (Figure 1) shows the peaks that appear at diffraction angles ( $2\theta$ ) which is the result diffractogram certain crystals of anatase TiO<sub>2</sub>. This is reinforced by the presence of peaks at  $2\theta = 25.35^\circ$  (D101 = 3.5091 Å),  $2\theta = 37.90^\circ$  (d004 = 2.3679 Å),  $2\theta = 48.10^\circ$  (D200 = 1, 8874 Å),  $2\theta = 54.15^\circ$  (D105 = 1.6931 Å), and  $2\theta = 54.95^\circ$  (D211 = 1.6674 Å) which is a regional characterization of anatase TiO<sub>2</sub> in accordance with the standard JCPDS No. 782-486.



**Figure 1. XRD technical TiO<sub>2</sub> (a) before treatment Ball milling (b) after a treatment of ball milling at a speed of 1000 rpm for 4 hours**

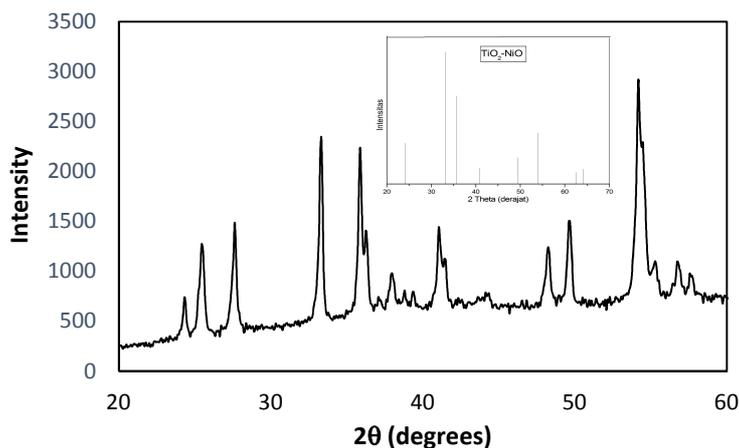


Figure 2. The spectra of X-ray diffraction (XRD)  $\text{TiO}_2\text{-NiO}$  synthesized

XRD analysis results for the electrode Ti /  $\text{TiO}_2\text{-NiO}$  synthesis results can be shown in Figure 2, the figures show a diffractogram electrode Ti /  $\text{TiO}_2\text{-NiO}$ . From Figure 2 known to appear peak - peak indicating the presence of NiO as indicated by the peak in the region  $2\theta = 43^\circ$  ( $D_{200} = 2.08 \text{ \AA}$ ) according to the standard JCPDS No. 471-049. In addition to the emergence of NiO produced also  $\text{NiTiO}_3$  which coincided with NiO. Peaks that characterize the phase  $\text{NiTiO}_3$  is tops in the region  $2\theta = 24^\circ$  ( $d_{012} = 3.6584 \text{ \AA}$ ),  $2\theta = 33^\circ$  ( $D_{110} = 2.6911 \text{ \AA}$ ),  $2\theta = 49^\circ$  ( $d_{024} = 1.8356 \text{ \AA}$ ), and  $2\theta = 57^\circ$  ( $d_{018} = 1.5969 \text{ \AA}$ ) in accordance with JCPDS No. 753-757.

The second achievement in this study was the composite of  $\text{TiO}_2\text{-NiO}$ . FTIR spectra of  $\text{TiO}_2\text{-NiO}$  composite after calcination of  $700^\circ \text{C}$  is shown in Figure 3. Composite  $\text{TiO}_2\text{-NiO}$  calcined at this temperature has been selected rutile ratio is best based on previous research that has been done (Wahyuningsih *et al.*, 2014). On the emerging new absorption spectra at wave number  $438.82 \text{ cm}^{-1}$ , which shows the Ni-O bond vibrations resulting from the addition of NiO on  $\text{TiO}_2$  according to research conducted Motlagh *et al.* (2011). With the uptake identifies nickel oxide has been formed.

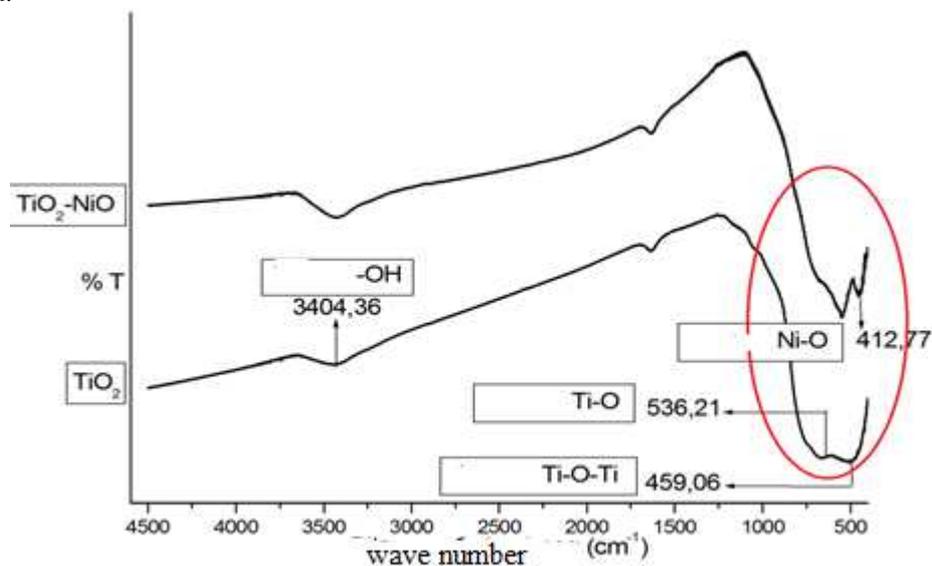


Figure 3. Spectra of FTIR (a)  $\text{TiO}_2$  dan (b)  $\text{TiO}_2\text{-NiO}$

$\text{TiO}_2\text{-NiO}$  solid morphology by TEM analysis shown in Figure 4. Morphology of  $\text{TiO}_2\text{-NiO}$  solid is spherical. TEM bright areas (bright field), which shows  $\text{TiO}_2$  dominant areas, while the darker areas TEM showing the area dominant NiO. While SEM micrograph of the electrode Ti /  $\text{TiO}_2\text{-Ni}$  is shown in Figure 5.

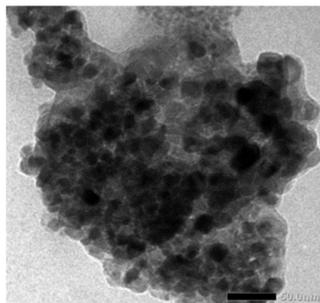


Figure 4. Morphology TEM photoanoda composite material  $\text{TiO}_2\text{-NiO}$  synthesized

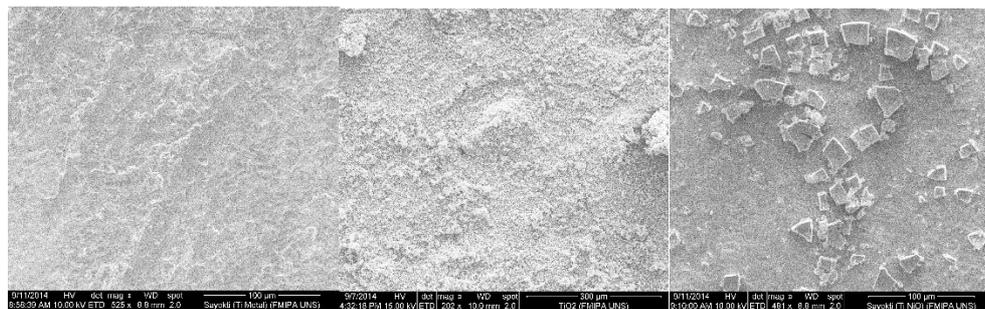


Figure 5. Morphology photoanoda material (a) SEM commercial electrode rod Ti (b) SEM fotoanoda Ti /  $\text{TiO}_2$  (c) SEM fotoanoda Ti /  $\text{TiO}_2\text{-Ni}$

Transmittance spectra dye waste biodeinking results can be seen in Figure 6. The results in Figure 6 shows the increase in transmittance dye biodeinking waste after being processed in the reactor photoelectrocatalitic. The increase in transmittance seen at the highest voltage of 6V. The increase in transmittance indicates that there has been a maximum degradation of dye wastewater results biodeinking

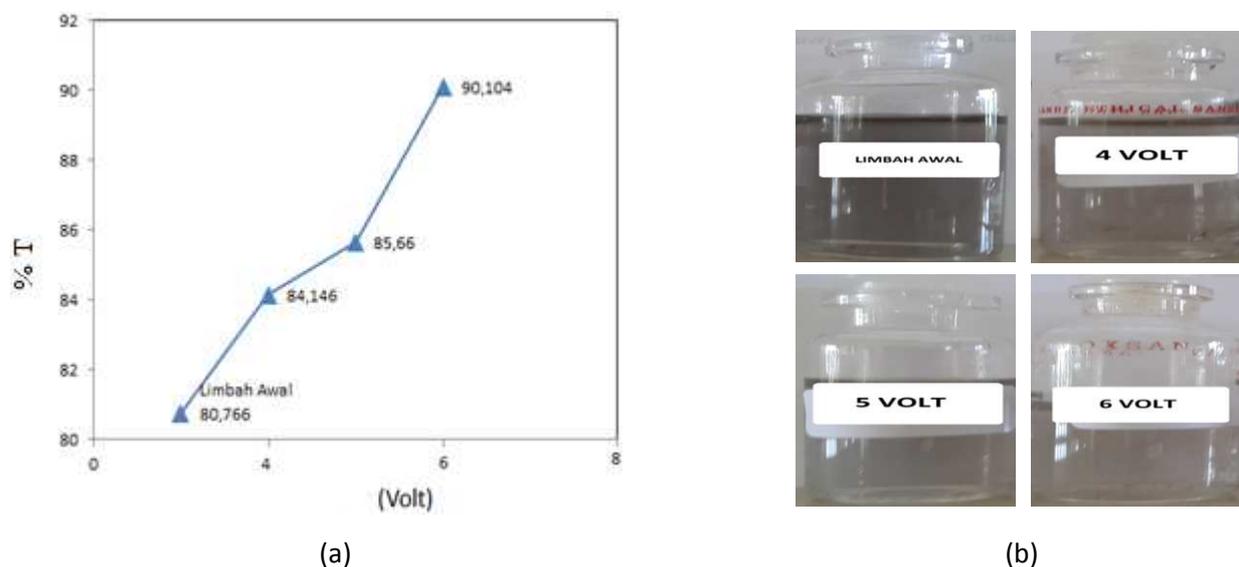
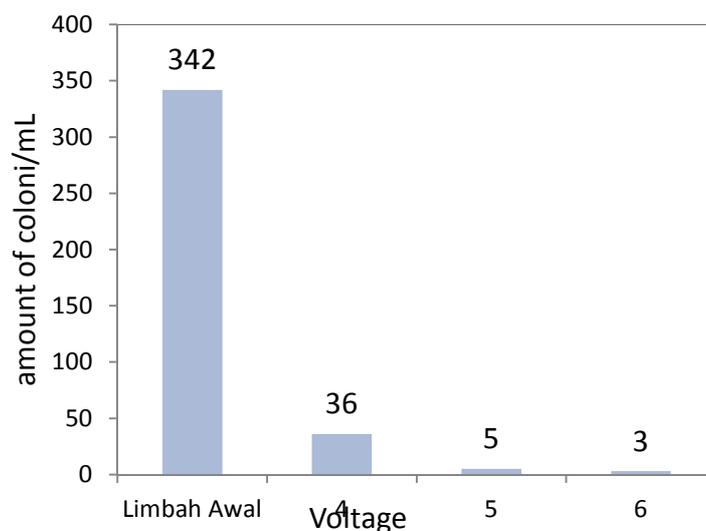


Figure 6. Results photoelectrodegradation biodeinking waste (a) flow rate of 3 mL / min at voltage variations (b) changes color (turbidity) before and after treatment

While the number of bacterial degradation products is shown in Figure 7. Degradation of bacteria showed that the larger the voltage is used, the number of bacteria contained in the decrease.



**Figure 7. Results photoelectrodegradation against the number of bacteria in waste**

The relationship between voltage with a percentage degradation (D) is greater if the voltage then the price of D are also getting bigger. At the time of visible light illumination can excite an electron from the dopant material NiO there are some electrons combine with holes (h<sup>+</sup>), with the provision of a bias potential to the electrode can prevent the occurrence of electron-hole recombination so that the flow of electrons can continue. Excited electrons exist in conducting this bond (ECB) immediately reacts with O<sub>2</sub> to produce radical O<sub>2</sub><sup>-</sup>. The ECB will initiate the reduction reaction at the semiconductor surface.



Selanjutnya O<sub>2</sub><sup>-</sup> can react intensively with the dye waste and bacteria in waste biodeinking results are closer to the anode (photoanoda Ti / TiO<sub>2</sub>-NiO). Semiconductors TiO<sub>2</sub> can accept electron injection from NiO hereinafter may also react with O<sub>2</sub> to produce radical O<sub>2</sub><sup>-</sup> Formation h<sup>+</sup> (holes) on the photochemical reaction called h<sup>+</sup> + vb, can initiate the oxidation reaction. The reaction of oxidation-reduction reaction that occurs is h<sup>+</sup> + vb → dapat oxidize water or hydroxyl groups on the dye waste biodeinking that teradsorb on the surface, and the ECB may reduce teradsorb oxygen to form superoxide anion radicals and hidroksiperoksida. h<sup>+</sup> + vb and the ECB can produce hydroxyl radicals which is a strong oxidizing to oxidize most organic compounds into water, minerals, and carbon dioxide (Gunlazuardi, 2011).

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