Synthesis of CNS, ZnO/CNS and ZnCr$_2$O$_4$/CNS composites from patchouli biomass by using microwave for remediation of pesticide contaminated surface water in paddy field

T Setianingsih$^{1,*}$, D Purwonugroho$^1$, YP Prananto$^1$

$^1$Department of Chemistry, Brawijaya University, Jl. Veteran 169 Malang 65145, Indonesia

*Correspondent author: tutiksetia@ub.ac.id

Abstract. Patchouli biomass is a potential precursor for CNS synthesis. In this research, the patchouli was pyrolyzed using the microwave. The purpose of this research is to study the effect of microwave energy and activator toward physicochemistry of CNS and composite (ZnO/CNS) and application of ZnCr$_2$O$_4$/CNS for the pesticide polluted surface water remediation in paddy field. In the process, the biomass was pyrolyzed at four and 8W with and without the ZnCl$_2$ activator. The products were blended and evaporated to obtain CNS and ZnO/CNS. The products were characterized using FTIR spectrometry, XRD, and dispersion test. The composites were used to synthesize ZnCr$_2$O$_4$/CNS at 600W in the microwave. The composites were used for buthylphenylmethyl carbamate pesticide degradation test (BPMC) for 48 h with H$_2$O$_2$ oxidation. The FTIR spectra indicated better carbonization for products taken using an activator at both microwave energies. The X-ray diffractograms showed the turbostratic structure of carbon obtained at 4W pyrolysis (with activator), meanwhile 8W pyrolysis (without activator). ZnO and turbostratic carbon structures were shown by the product of 8W pyrolysis with activator. The calcined composite indicated ZnCr$_2$O$_4$/CNS. The degradation test showed that ZnCr$_2$O$_4$/CNS(8W) catalyst decreased the BMPC concentration almost three times that of the composite (4W).

Keywords: Composite, microwave, patchouli biomass, pesticide, surface water

1. Introduction

Pesticides can be classified based on the target organism. It includes insecticides (insects), herbicides (weeds), rodentine (rodents), fungicides (fungi), acaricides and miticides (arachnids such as ticks and mites) molluscicides (mollusks), bactericides (bacteria), avicides (bird pests), virucides (viruses), algicides (algae). Based on chemistry, pesticides are classified into four main groups, i.e., organochlorines, organophosphorus, carbamates, and pyrethrin/pyrethroids [1].

Among them, organochlorine and organophosphate are very toxic and have long persistence. Carbamate and piretroide are easier for degradation but keep potentially accumulated [2]. Accumulation of pesticides lasts in both water and soil. It can be toxic and kills animals, but on the other side can create pest resistance. The other risks of pesticides include birth disability, genetic mutation, brain damage, and cancer. Pesticide residue potentially contaminates various agricultural products [2,3].
The pesticide pollutant problem can be overcome by using nanocarbon adsorbents. Nanocarbon or carbon nanomaterial has a particle size of 1-100 nm [4]. The small size of this carbon particle makes it easier for farmers to spray it on paddy fields together with liquid fertilizer.

Nano carbons have been prepared using the pyrolysis method of hydrothermal [5-8], conventional thermal [6,9-10], and microwave thermal [9,11]. Hydrothermal carbonization (HTC) is a thermo-chemical process that lasts in a sub-critical liquid water medium at a temperature of 180-250°C. This method applies lower operating temperature than the pyrolysis process by the conventional furnace [12]. Hydrothermal pyrolysis usually uses acids, bases, metallic salts, or water substances as green catalysts. To transform the biomass into carbon, a chemical reaction in hydrothermal pyrolysis is complex, such as condensation, hydrolysis, dehydration, and decarboxylation. The hydrothermal carbonization (HTC) process is conducted in the autoclave. A vessel made from teflon inside and stainless steel outside. By this autoclave, pressure can be created autogenously. Hydrothermal pyrolysis is more flexible than dry pyrolysis. The wet biomass can be used to exclude the pre-drying process before the HTC treatment [13].

A microwave (MW) is electromagnetic radiation that has a frequency of 300-300000 MHz. Electromagnetic radiation passes through the material and stimulates molecule oscillation which produces heat. Microwave heating produces heat in the entire material at a high rate of reaction. It leads to a fast reaction [14]. The property of microwave heating is different from conventional heating. Conventional heating involves the usage of a furnace that heats the walls of the reactors by conduction. It needs a longer time to heat material than the microwave because the microwave penetrates inside the material, and the heat is generated by direct interaction of microwave and material [15]. Consequently, a microwave has a short duration of pyrolysis [5, 6, 7, 9, 10]. Nanocarbon can be produced from biomass. The biomass is a lignocellulosic material rich in cellulose, lignin, and hemicellulose, i.e., 20–40, 40–60, and 10–25 wt.%, respectively [16]. Biomass can be transformed to carbon using thermal, biological, and physicochemical processes [13]. Thermally, stages of biomass pyrolysis involve moisture evolution and decomposition of three lignocellulose components [16]. Some biomasses have been used as precursors of the nanocarbon using the hydrothermal-microwave method, such as patchouli, rice husk, and sugarcane leaf [17]. The other research has used those same biomasses and two more others, including sawdust and coconut husk, by microwave pyrolysis [18]. Oxide metal nanoparticle was also synthesized using microwave calcination, such as ZnO [19]. Nanoparticles form the typical colloidal systems, consisting of solvent as the dispersing phase and nanoparticle as the dispersed phase [20]. The colloidal suspension of nanoparticles that are less than 100 nm are dispersed in base fluids such as water is called nanofluid [21]. Some techniques can be used to conditionate nano size of carbon nanomaterial to form dispersion system, i.e., a technique of sonication [17, 22, 23] and blending [17]. Based on the stability test of carbon colloid, the blending technique resulted in better stability of carbon colloid than sonication [18].

Degradation of pesticides in the soil can be conducted naturally by microorganisms such as bacteria, fungi, and actinomycetes are the essential group of degraders. The pesticide degradation by biological oxidations is accomplished enzymatically, primarily by the mixed function oxidases (utilizing cytochrome P450), the flavin-dependent monooxygenase, and monoamine oxidase [24]. Chemical degradation can be performed friendly using oxidator such as peroxide acid. This oxidator is an additive in the liquid fertilizer for removing fungi or bacteria which inhibit plants growth [25]. Peroxide acid is safe for fish and can improve DO in a water environment [26].

The composites of MFe$_2$O$_4$/CNM and MCr$_2$O$_4$/CNM (M = Zn, Ni, Mn) have been used for catalytic degradation of BPMC pesticide. CNM was synthesized with hydrothermal-microwave methods using biomass such as sugarcane leaf, patchouli, rice husk, and wood char. Both ZnCr$_2$O$_4$/CNM and ZnFe$_2$O$_4$/CNM gave good catalytic activity in dark degradation [17]. In this research, the patchouli biomass was pyrolyzed using a microwave with a ZnCl$_2$ activator. The product was used to synthesize ZnCr$_2$O$_4$/CNM. The final product was applied as the catalyst for the degradation of pesticides.
2. Materials and Methods

2.1. Material of research
This research used patchouli biomass as a precursor of carbon. Some chemicals were needed, such as ZnCl\(_2\) (Merck), KOH (Merck), CrCl\(_3\).6H\(_2\)O (Merck), H\(_2\)O\(_2\) 3% (techniques), BPMC (buthylphenylmethyl carbamate) techniques, distillate water.

2.2. Procedures of research

2.2.1. Synthesis of ZnO/CNS and ZnCr\(_2\)O\(_4\)/CNS
The dry patchouli biomass was shieved by tea shiever then mixed with ZnCl\(_2\) at a ratio of 5:1 and pyrolyzed at 400, 600, and 800W for 50 minutes. The products were blended in water to form colloids. The colloids were used for the test of stability and evaporated to obtain ZnO/CNS nanocomposite. For comparison, the CNS was prepared in the same procedure without ZnCl\(_2\). Each ZnO/CNS composite (1.0 g) was further calcined at 400 and 800 W after mixing with some substances including KOH (1.34 g), ZnCl\(_2\) (0.20 g), CrCl\(_3\).6H\(_2\)O (0.79 g), and distillated water (1 mL), then calcined by microwave for 5 minutes at 600 W to produce ZnCr\(_2\)O\(_4\)/CNS composite.

2.2.2. Characterization
The ZnO/CNS products were characterized with some methods such as FTIR spectrophotometry (functional group), X-ray diffraction (crystal structure), SEM (morphology), and optic photography, and TDS meter for the test of colloid stability. The final product, ZnCr\(_2\)O\(_4\)/CNS was characterized with FTIR spectrometry.

2.2.3. Application of ZnCr\(_2\)O\(_4\)/CNS composite for dark degradation reaction of pesticide
Before application, paddy soil was deactivated by drying at 200°C for five h and conditioned to particle size > 200 mesh and homogenized. The pesticide (BPMC) solution was prepared by dissolving the concentrated BPMC (500 g/L; 0.5 mL) to 500 mL. The oxidator H\(_2\)O\(_2\) solution (0.15%) was prepared by dissolving more concentrated H\(_2\)O\(_2\) (3%; 25 mL) to 500 mL. Test of dark pesticide degradation in the soil was conducted by procedures presented in Table 1 as follows:

| No. | Purpose                                                   | Code   | Experiment                                         | Indicator |
|-----|-----------------------------------------------------------|--------|----------------------------------------------------|-----------|
| 1.  | Test of pesticide adsorption by the deactivated soil      | BT     | Dry soil (5 gram) + BPMC solution (0.5g/L; 25 mL) + water (10 mL), saved in the dark for 5 days. | TOC       |
| 2.  | Test of pesticide degradation by a catalytic oxidation reaction with H\(_2\)O\(_2\) - ZnCr\(_2\)O\(_4\)/CNS | CTNMZX | Dry soil (5 gram) + BPMC solution (0.5g/L; 25 mL) + H\(_2\)O\(_2\) solution (0.15%; 10 mL) + composite (0.1 g), saved in the dark for 5 days. | TOC       |

TOC of filtrates were measured using mini-TOC meter. The activity of catalytic oxidation in degradation reaction was calculated from the difference of TOC infiltrate after the contaminated soil treatment with composite - H\(_2\)O\(_2\) (CTNMX) and the contaminated soil without treatment (BT), as follows:

\[
\text{Activity of catalytic oxidation} = \frac{[\text{TOC}_{\text{BT}} - \text{TOC}_{\text{CTNMX}}]}{\text{TOC}_{\text{BT}}} \times 100\% 
\] (1)
3. Results and Discussions

3.1 Material transformation

Patchouli biomass was used as a precursor for the synthesis of ZnO/CNS. Besides that, the biomass was analyzed to determine its content. The analysis laboratory determined lignocellulosic components in the patchouli biomass for public service in the Department of Chemistry Brawijaya University. The biomass photograph and result of the analysis are presented in Figure 1. Based on the analysis, it is known that lignocellulosic content in the patchouli biomass is in a sequence of cellulose > lignin > hemicellulose. Those three substances are different macro molecules with different structures, but all are organic polymers rich in hydroxide functional groups. Among them, only lignin contains the aromatic structures which are linked by oxygen or carbon atoms, whereas the two others consist of alkane cyclers that are linked by oxygen atoms only [27].

![Patchouli biomass and component in patchouli biomass](image1.png)

**Figure 1.** Patchouli biomass and component in patchouli biomass

The pyrolysis process of the biomass using a microwave for 50 minutes resulted in the black products named activated carbon (Figure 2). This carbon can be called activated carbon because ZnCl$_2$ was used as the activator. The role of this salt is a dehydrating agent, which improves reactions in pyrolysis and reduces the side product such as tar [28]. No washing was conducted so that the pyrolysis product contains ZnO due to the reaction between ZnCl$_2$ and gasses emitted by the reaction. Based on color of the carbons, the carbon which was pyrolyzed without the activator, especially at the lowest energy, i.e., 400 W (NM4), has the lightest color (brownies black). The carbonization reaction is worst because the process was conducted at the lowest energy or the lowest temperature.

![Activated carbon from pyrolysis of the patchouli biomass by microwave](image2.png)

**Figure 2.** Activated carbon from pyrolysis of the patchouli biomass by microwave

The Efforts to optimize the nano size, the carbons were blended in water to form the colloid or dispersion systems. The mechanical force of the blending technique caused the collision of the carbon particles. The particles broke and formed the smaller ones. The carbon colloids which were resulted from blending are presented in Figure 3.
Figure 3. Dispersed system of CNS in water by blending

Figure 4 is the process of checking the concentration of carbon dispersed in a colloids system and measuring the value of colloids TDS.

![TDS measurement process](image)

Figure 4. TDS measurement process (left) and data (right) of the carbon colloids

The TDS data shows that pyrolysis with the ZnCl$_2$ activator causes TDS of the carbons (NMZ4, NMZ6, NMZ8) higher than without an activator. It means that usage of activator causes a higher concentration of the carbon colloid than without the activator. The role of the activator, which prevents the side products (tar) caused an amount of the activated carbon is more than without activator so that concentration of the colloid and TDS are large.

To get the nano carbon with ZnO impurity or ZnO/CNS, the colloids were evaporated. The composites as a result of the evaporation process are shown in Figure 5.

![Nanocarbon from pyrolysis](image)

Figure 5. Nanocarbon from pyrolysis of patchouli biomass by microwave

All evaporated carbons show smoother powder than before dispersion. It is visual proof that the blending process reduced the carbon particles. The color of the composites is matched the activated carbon before the dispersion process.

The ZnO/CNS was used to synthesize ZnCr$_2$O$_4$/CNS by calcination of ZnO/CNS, KOH, ZnCl$_2$, CrCl$_3$.6H$_2$O mixture. During calcination process, there are 2 kinds of reactions, i.e reaction of the substances thermally to form spinel (ferrite) ZnCr$_2$O$_4$. The possible stoichiometric reaction as follows:

$$\text{ZnO} + 2\text{CrCl}_3.6\text{H}_2\text{O} + \text{KOH} + \text{ZnCl}_2 \xrightarrow{\Delta} \text{ZnCr}_2\text{O}_4 + 7\text{HCl (g)} + \text{KCl} + \text{ZnO} + 9\text{H}_2\text{O (g)}$$
Another reaction is the further activation of carbon by inorganic substances thermally. The products after calcination are shown in Figure 6.

![Figure 6. The final product (Composite of ZnCr$_2$O$_4$/CNS)](image)

Both final products keep looking black. The ferrite content in the products is too little to impact the ZnO in the intermediate product was related with KOH, CrCl$_3$, and ZnCl$_2$ thermally to form a spinel substance ZnCr$_2$O$_4$. This substance was not characterized but can be justified as ZnCr$_2$O$_4$ because based on previous research [17], all products which were prepared by involving various M(II) and M(III) indicated spinel MCr$_2$O$_4$, MFe$_2$O$_4$, and MAl$_2$O$_4$. Between ferrite substance and carbon surface are not reacted chemically. Both are only in attraction forces such as hydrogen bonds.

![Figure 7. FTIR spectra of CNS and ZnO/CNS from patchouli biomass by pyrolysis using microwave](image)

### 3.2. Functional groups of ZnO/CNS composite

The ZnO/CNS composites have been characterized using FTIR spectrometry to identify their functional groups. The Characterization was conducted in the Laboratory of Central Mineral and Advance Material, State University of Malang (LSUM). The codes of samples on the spectra out and in of the brackets are given by main author and LSUM, respectively. The highest (800 W) and the
lowest (400 W) energies were considered to influence microwave energy toward the functional groups significantly. The FTIR spectra of the composites are presented in Figure 7.

Generally, the carbons which were prepared without an activator show sharper FTIR spectra than with an activator. The existence of those sharper bands indicates that the carbonization reaction without an activator is worse than with the activator. So that the functional groups on the edges of the graphene layers are still many, and the spectra bands are sharper. However, the different microwave energy does not have too significant an influence on FTIR spectra.

The sharp FTIR spectra of the carbon were prepared without an activator. The bands related to oxy functional groups can be interpreted as follows: the -OH functional groups of phenol or hydrate at about 3500 cm⁻¹, C=O at 1700 cm⁻¹, and C-O at about 1000 cm⁻¹. Those bands match with vibrations of the functional groups in structures of lignin, cellulose, and hemicellulose, such as O-H stretching of phenol at 3000 - 3600 cm⁻¹, C=O stretching at 1700-1730 cm⁻¹, C-O stretching at 1215 cm⁻¹ (phenol), C-O stretching of pyranose ring skeletal at 1170 and 1082 cm⁻¹ [16]. The existence of those oxy functional groups indicates that the carbonization reaction is not completed.

Nonoxy functional groups detected in FTIR spectra of the carbon are as aliphatic C-H at about 2900 cm⁻¹, aromatic C=C at 1600 cm⁻¹, and C-H out of a plane in graphene aromatic layer at about 800 cm⁻¹. All of those were also detected in the analysis of lignin, cellulose, and hemicellulose, including C–H stretching (alkyl, aliphatic) at 2860–2970cm⁻¹, C=C stretching of benzene ring 1613 at 1632, and C=C stretching for aromatic skeletal mode at 1450 (w) and C-H stretching of C–H aromatic hydrogen at 700–900 (m) [29].

![Figure 7. FTIR spectra of the composites.](image)

**Figure 7.** FTIR spectra of the composites.

**Figure 8.** X-ray diffractograms of nanocarbon from patchouli biomass by microwave pyrolysis

### 3.3. Crystal structure of the carbon and composite

Identification of functional groups is not enough for the Characterization of carbon material, especially related to the crystal structure of a material. This property can be detected by XRD method. The Characterization was performed in LSUM too. The samples were coded by author and by LSUM (in the bracket). Patterns of the carbons and composites’ X-ray diffractograms are presented in Figure 8.

The patchouli biomass X-ray diffractogram pattern in Figure 7 is similar to the X-ray diffractogram of biomass and cellulose [30-31]. After pyrolysis at 800 W without an activator (TNM8), the X-ray diffractogram reduces the main peak, which indicates that biomass has been
This pattern of carbon is similar to the pattern of CNT [32]. Usage of activator at the same temperature shows a different pattern, i.e., the emergence of sharp peaks indicating oxide metal (ZnO) from the reaction of activator and oxy gas released from carbonization reaction. This emergence lasted together with much reduction of the carbon’s wide peak. When the temperature was decreased at 400 W with the activator the main peak kept high, and relatively no peaks of ZnO. Both phenomena indicate degradation of carbon in 800 W and a reaction of metal oxide formation.

3.4. Morphology of ZnO/CNS composite

Morphology of composite surface was characterized with SEM. The SEM image of the composite is shown in Figure 9. The main author and LSUM gave the code of sample (in the bracket). The choice of the sample was based on the emergence of ZnO significantly in Characterization by XRD. The SEM image of the composite shows an irregular pattern. White particles of the solid indicate ZnO on the carbon surface.

![SEM image of ZnO/CNS composite](image)

Figure 9. SEM image of ZnO/CNS from patchouli biomass by pyrolysis using the microwave at 800W using activator ZnCl$_2$

![Test of carbon colloid stability](image)

Figure 10. Test of carbon colloid stability
3.5. Colloid stability of ZnO/CNS stability

The stability of the carbon colloid is an essential factor in the application of the composite as an additive of liquid fertilizer. It was performed in this research by observing the colloid from 10.11 AM to 12.28 PM. Changing of the colloid appearance was documented by photography as presented in Figure 10.

Figure 10 shows that the colloids of carbons from pyrolysis without activator show more concentration than activator at 11.15 AM and 12.28 PM or after staying 1 and 2 h. It means that the carbons which were prepared without an activator can form more stable colloids. Different concentrations of the colloids cause this different stability after the blending process. Based on Figure 5, the colloids of the carbons by pyrolysis with activator had more concentrated than without activator. Colloidal agglomeration is easy to occur if the colloid concentration is large, the space between the carbon particles is small, and strong attraction between the particles. Based on the FTIR spectra, the surface of the carbons can interact with each other by hydrogen bond and London force.

3.6. Functional group of ZnCr$_2$O$_4$/CNS

The final product in this research was characterized with FTIR spectrometry to identify their functional groups. Their functional groups were identified using FTIR spectrophotometry (Figure 11). The measurement of the FTIR spectra in Instrument Laboratory in Department of Chemistry Brawijaya University. No additional codes of samples from the laboratory. Based on XRD characterization of the final product taken with the same procedure but different biomass (rice husk), the final product was ZnCr$_2$O$_4$/CNS [18]. The different biomass gave the same crystal structure and crystallinity for synthesizing MnCr$_2$O$_4$/CNS, using hydrothermal - microwave method [17]. So that, the final product in this research was predicted as ZnCr$_2$O$_4$/CNS. The functional groups of the final composite were based on reaction equation (1). The calcination gives possible functional groups of ZnO and ZnCr$_2$O$_4$ such as M-O and CNS such as -OH, C=O, C-O, C-H out of a plane. These functional groups of the CNS are products of further activation by salts and bases during the calcination process. Those base and salts such as KOH and ZnCl$_2$ further activated carbon [33-35], or CrCl$_3$ oxidized the carbon [36].

To prepare composite of ZnCr$_2$O$_4$/CNS, the mixture of base (KOH), salts (CrCl$_3$.6H$_2$O, ZnCl$_2$), and intermediate composite (ZnO/CNS) have been calcined to get the final composite of ZnCr$_2$O$_4$/CNS. The CNS is eroded by reaction with KOH and leaves voids on its frame. This reaction involves a dehydration reaction of KOH thermally and releases water vapor. This H$_2$O molecule reacts with the carbon surface to form hydrogen gas. The activation reaction of carbon surface by KOH is as follows [29]:

$$4\text{KOH} \rightarrow 2\text{K}_2\text{O} + 2\text{H}_2\text{O}$$
$$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$$
$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$$

$$4\text{KOH (s)} + \text{C(s)} \rightarrow 2\text{K}_2\text{O (s)} + 2\text{H}_2(\text{g})$$

The ZnCl$_2$ activator is a template that forms pores and an acidic catalyst that supports carbonization reaction [9]. In chemical activation, carbonization and activation work simultaneously [28]. A low melting point (283–293 °C) allows ZnCl$_2$ has better contact with the carbon surface [33]. Chemical activator dehydrates precursor for carbonization and aromatization to form pores and surface area [37]. The dehydration influences pyrolytic decomposition, which impedes tar formation and improves carbon products [38].

Interpretation of spectra functional groups in FTIR spectra of the final products is listed in Table 2. Based on Figure 11 and interpretation in Table 2, the FTIR spectra of the ZnCr$_2$O$_4$/CNS composite from the carbon by pyrolysis at 400 W (CTNMZ4) tends to show sharper bands in vibrations in carbon structure than at 800 W (CTNMZ8), especially related to -OH, C=O, and C-O. 800 W gave higher temperature, which potentially increased the activation process by some substances of base and salts.
The M-O band of the ZnCr$_2$O$_4$/CNS composite related to the 400 W (CTNMZ4) spectrum is also sharper than the other composite related to the 800 W (CTNMZ8) one. This phenomenon has happened possibly because evaporation of salts which achieved a boiling point in the temperature of carbonization.

![Figure 11. FTIR spectra of the ZnCr$_2$O$_4$/CNS composites based on CNS from pyrolysis at 400 W (CTNMZ4) and 800W (CTNMZ8)](image)

**Table 2. Interpretation of composites’ FTIR spectra**

| ZnCr$_2$O$_4$/CNS composites | CTNMZ4 | CTNMZ8 | v (cm$^{-1}$) | Interpretation | References |
|------------------------------|--------|--------|--------------|----------------|------------|
| CTNMZ4                       | 3134.81 | 3064.93 | ~ 3500       | stretching vibration of OH-bonds (alcohol, phenol, and carboxyl groups) | [12]        |
| 1654.41                      | 1661.54 | 1693.5 |               | stretching vibrations of C=O | [39]        |
| 1466.15; 1440.82             | 1437.62; 1396.26 | 1450−1112 |               | stretching vibrations of C=C in aromatic groups | [34]        |
| 1006.91                      | 1108.17 | 1091;787 |               | stretching vibration bands of C-O indicated the presence of carboxylic acid and other oxygen containing functional groups | [8]         |
| 889.96; 623.25               | 842.89; 666.04; 620.40 | 700−900; 618 | aromatic hydrogen | single bond stretching and other deformation bands, including C–H vibration at the aromatic structure | [16] [34] |
| 527.7                        | 482.06  | 475    | 540          | M-O stretching | [19] [40] |
3.7. Test of pesticide degradation

To support of characterization data for synthesized material, a degradation test of pesticide was conducted. This test result can describe how the performance of the composite as a catalyst in pesticide degradation. BPMC pesticide was used, and the wet paddy soil was chosen as media for an experiment. Filtrates and residues of wet soil after the degradation test are shown in Figure 12. TOC was the measurement for each sample using a mini TOC meter (Figure 13).

![Figure 12. Filtrate and residue of solid (T) after test of pesticide (B) degradation](image1.png)

![Figure 13. Measurement of TOC infiltrate after test of pesticide degradation using mini TOC meter](image2.png)
TOC infiltrate after the dissolution was measurement using a mini TOC meter and presented in Figure 14 as TOC and percentage TOC reduction. The TOC reduction percentage describes the activity of catalytic oxidation.

Figure 14 shows three different conditions, i.e., the pesticide was oxidized without composite catalyst (BT), with composite which was prepared by involving pyrolysis at 800 W (CTNMZ8) and 400 W (CTNMZ4). Based on the graph, the CTNMZ8 gave a % TOC reduction more than two times. It means that CTNMZ8 has catalytic activity larger than CTNMZ4. The degradation reaction of pesticide is assumed same as DNA damage reaction catalytically by H$_2$O$_2$ using Cr(III) catalyst. The Cr(III) cations reduce H$_2$O$_2$ to form OH$^-$ Radicals and the Cr(III) are oxidized to form reactive Cr(IV) [41]. The radicals may attack the pesticide molecules to form more specific degradation products [42].

4. Conclusions
Synthesis of CNS and the composites including ZnO/CNS and ZnCr$_2$O$_4$/CNS was conducted. The chemical activator of ZnCl$_2$ made darker carbon products, more concentrated colloids, less stable colloids, less functional groups of carbon surfaces, and higher crystallinity of ZnO in the intermediate product. Increasing energy gave no significant different functional groups of ZnO/CNS but decreased functional groups of ZnCr$_2$O$_4$/CNS. The higher the microwave energy, the lower TDS of the carbon colloids, the larger catalytic activity of ZnCr$_2$O$_4$/CNS in dark degradation of pesticide.

Acknowledgment
We thank Brawijaya University for Hibah Doktor 2020 (Contract number of 42UN10.F09/PNr2020) to perform our research.

References
[1] Zacharia and Tano J 2011 Identity, Physical and Chemical Properties of Pesticides In: Pesticides in the Modern World - Trends in Pesticides Analysis, ed M Stoytcheva (UK: InTech) http://www.intechopen.com/books/pesticides-in-the-modern-world-trends-pesticidesanalysis/identiq1ty-physical-and-chemical-properties-of-pesticides
[2] Ardiwinata AN dan Nursyamsi D 2012 Pangan 21 (1) 39-58 https://doi.org/10.33964/jp.v21i1.103
[3] Fitriadi BR dan Putri AC 2016 Jurnal Rekayasa Kimia dan Lingkungan 11(2) 61-71 https://doi.org/10.23955/rkl.v11i2.4950
[4] Zaytseva O and Neumann G 2016 Chem. Biol. Technol. Agric. 3(17) 1-26 10.1186/s40538-016-0070-8
[5] Hoan BT, Tam PD, Pha VH 2019 Hindawi Journal of Nanotechnology 1-9 https://doi.org/10.1155/2019/2852816
[6] Adewumi GA, Revaprasadu N, Eloka-Eboka AC, Inambao FL and Gervas CA 2017 Proceedings of the World Congress on Engineering and Computer Science (WCECS) vol 2
[7] Liu Y, Liu Y, Park M, Park SJ, Zhang Y, Akanda MR, Park BY dan Kim HY 2017 *Carbon Letters* **21** 61-67 https://doi.org/10.5714/CL.2017.21.061

[8] Carvalho J, Santos LR, Germino JC, Terezo AJ, Moreto JA, FJ and Freitas RG 2019 *Materials Research*. **22**(3) 1-8 http://dx.doi.org/10.1590/1980-5373-MR-2018-0920

[9] Huang YF, Chiuheu PT, Shih CH, Lo SL, Sun L, Zhong Y and Qiu C 2015, *Energy* **84** 75-82 https://doi.org/10.1016/j.energy.2015.02.026

[10] Inyang M, Gao B, Zimmerman A, Zhang M and Chena H 2014 *Chemical Engineering Journal*. **236** 39–46 https://doi.org/10.1016/j.cej.2013.09.074

[11] Schwenke AM, Hoeppener S, Schubert US 2015 *Adv. Mater.* **27** 4113–4141 https://doi.org/10.1002/adma.201500472

[12] Larasati TD, Prakoso T, Rizkiana J, Devianto H, Widiatmoko P and Nurdin I 2018 *1st International Symposium of Indonesian Chemical Engineering (ISIChem) IOP Conf. Series: Materials Science and Engineering*. 543 (UK: IOP Publishing Ltd) p.1-8 doi:10.1088/1757-899X/543/1/012031

[13] Chowdhury ZZ, Krishnan B, Sagadevan S, Rafique RF, Hamizi NAB, Wahab YA, Khan AA, Johan RB, Al-douri Y, Kazi SN, and Shah ST 2018 *Nanomaterials*. **8**(597) 1-19 doi:10.3390/nano8080597

[14] Taylor M 2005 Developments in Microwave Chemistry (London UK: Evalueserve) pp.5-9 https://www.rsc.org/images/evaluserve_tcm18-16758.pdf

[15] Saxena VK and Chandra U 2011 *Microwave Synthesis: a Physical Concept, Microwave Heating, ed* Dr. Usha Chandra (Rijeka Croatia: InTech) http://www.intechopen.com/books/microwave-heating-microwave-synthesis-a-physical-concept

[16] Yang H, Yan R, Chen H, Lee DH and Zheng C 2007 *Fuel* **86** 1781–1788 https://doi.org/10.1016/j.fuel.2006.12.013

[17] Setianingsih T and Mutofin S 2019 Sintesis Karbon Nanomaterial dari Limbah Biomassa yang Dimodifikasi MFe₂O₄ Secara Green Technology Sebagai Campuran Pupuk Cair Untuk Remediator Tanah Sawah dan Saluran Irrigasi Tercemar Pesticida *Laporan akhir HPU* (Malang: Universitas Brawijaya) pp 1-123

[18] Setianingsih T, Purwonugroho D, Prananto YP 2020 Sintesis Nanokarbon dan Komposit Nanokarbon dari Biomassa dengan Metode Pirolisis Fasa Padat dengan Miwrowave - Sonikasi untuk Remediator Lahan Tanah Pertanian Tercemar Pestsisida *Laporan akhir Hibah Doktor Lektor Kepala* (Malang: Universitas Brawijaya)

[19] Pauzi N, Zain, NM and Yusof NAA 2019 *Bulletin of Chemical Reaction Engineering & Catalysis*. **14**(1) 182-188 doi:10.9767/bcrec.14.1.3320.182-188

[20] Milanovi´ M, Stijepovi´ I, Pavlovi´ V and Srdi´ V 2016 *Processing and Application of Ceramics*. **10** (4) 287–293 DOI: 10.2298/PAC1604287M

[21] Mahbubul M, Chong TH, Khaleduzzaman SS, Shahrul IM, Saidur R, Long BD and Amalina MA 2014 *Ind. Eng. Chem. Res.* **53** 6677–6684 https://doi.org/10.1021/ie500705j

[22] Bang JH and Suslick KS 2010 *Adv. Mater.* **22** 1039–1059 DOI: 10.1002/adma.200904093

[23] Hielscher T 2005 Ultrasonic Production of Nano - size Dispersions and Emulsions (France: ENS’05) 14-16 https://hal.archives-ouvertes.fr/hal-00166996/document

[24] Coats JR 1991 American Chemical Society *459*(2); 10-30 doi:10.1021/bk-1991-0459.ch002.

[25] Triyanto KBT 2016 *Manfaat Hidrogen Peroksida (H₂O₂) Bagi Tanaman* KabarTani.com https://kabartani.com/manfaat-hidrogen-peroksidadh2o2-bagi-tanaman. html

[26] Hany RCR 2014 *Efektivitas Pemberian Hidrogen Peroksida Terhadap Kualitas Media, Kelangsungan Hidup dan Pertumbuhan Benih Ikan Patin pangasius* sp. Skripsi Departemen Budidaya Perairan, Fakultas Perikanan dan Ilmu Kelautan IPB Bogor https://repository.ipb.ac.id/handle/123456789/74423

[27] Fu L, McCallum SA, Miao J, Hart C, Tudryn GJ, Zhang F, Linhardt RJ 2015 *Fuel* **14** 39–45 https://doi.org/10.1016/j.fuel.2014.10.039
[28] Marsh H and Reinoso R 2006 *Activated Carbon* (USA: Elsevier Sci.) https://3lib.net/book/599879/1fb3fe
[29] Yang HM, Zhang DH, Chen Y, Ran MJ and Gu JC 2017 *IOP Conf. Series: Earth and Environmental Science* 69 pp1-8 doi:10.1088/1755-1315/69/1/012051
[30] He W, Jiang S, Zhang Q, Pan M, 2013 *BioResources* 8(4) 5678-5689 https://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_08_4_5678_He_Nanofiber_Bambusa_2364
[31] Tsaneva VN, Kwapinski W, Teng X, Glowacki BA 2014 *Carbon* 80 617-628 https://doi.org/10.1016/j.carbon.2014.09.005
[32] Tyagi S, Verma P, Baskey HB, Agarwala RC, Agarwala V and Shami TC 2012 Ceramics *International* 38(6) 4561-4571 https://doi.org/10.1016/j.ceramint.2012.02.034
[33] Li B, Hu J, Xiong H and Xiao Y 2020 *ACS Omega* 5 9398–9407 https://dx.doi.org/10.1021/acsomega.0c00461
[34] Zubbri NA and Mohamed AR 2021 *Journal of Environmental Chemical Engineering* 9 1-12 https://doi.org/10.1016/j.jece.2021.105074
[35] Motlagh EK, Kolur NA, Sharifian S and Pirbazari AE 2021 *Biomass and Bioenergy* 144 1-17 https://doi.org/10.1016/j.biombioe.2020.105917
[36] Setianingsih T, Masruri, Ismuyanto B, 2018 *J. Pure App. Chem. Res.* 7(1) 60-69 DOI: 10.21776/ub.jpacr.2018.007.01.367
[37] McDougall GJ 1991 *(5,4),(998,994)*
[38] Viswanathan B, Neel PI and Varadarajan TK 2009 *Methods of Activation and Specific Application of Carbon Materials Thesis* (India: Indian Institute of Technology Madras) https://www.researchgate.net/profile/IndraPulidindi/publication/299393936_Methods_of_Activation_and_Specific_Applications_of_Carbon_Materials/links/56f3c7d808ae95e8b6cd2e46/Methods-of-Activation-and-Specific-Applications-of-Carbon-Materials.pdf
[39] Kristianto H, Lavenki Y and Susanti RF 2020 *IOP Conf. Series: Materials Science and Engineering* 742 p.1-6 doi:10.1088/1757-899X/742/1/012044
[40] Lemos de Peres M, Delucis RDA, Amico SC and Gatto DA 2019 *Nanomaterials and Nanotechnology* 9 1–8 https://doi.org/10.1177/1847980419876201
[41] Tsou T, Yang J 1996 *Chemico-Biological Interactions* 2(3) 133–153 doi: 10.1016/s0009-2797(96)03740-4
[42] Setianingsih T, Purwonugroho D, Prananto YP 2021 *ChemEngineering* 5(58) 1-21 https://doi.org/10.3390/chemengineering5030058