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Functionalization of Wood Char for Adsorption of Organic Contaminant

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ABSTRACT
Wood char is a carboneous pyrolized product which can used as both adsorbent and catalyst matrix. Quality of the wood char can be improved by activation, oxidation, and modification using oxide metals. Those treatment can increase its porosity, acid functional groups, and Lewis site, respectively, which increase its affinity toward organic substance. Purpose of this research is to study influence of functionalization of woodchar toward chemical property of thechar/carbon and adsorption of paracetamol. The activation of wood char was conducted by using KOH activator at 500 oC, the oxidation was performed using concentrate HNO3 solution at 80 oC, and modification by using Zn-Fe-LDH (Layered Double Hydroxide) and ZnFe2O4. Mol ratio of Fe(III)/Zn(II) was adjusted at 5:1. Adsorption test was performed by batch method (50 ppm of paracetamol; 0.1 g of adsorbent; at 200 rpm for 24h). Adsorption capacity was determined at the same condition, except at various concentration of paracetamol (10–100 ppm). Characterization using FTIR spectrophotometry confirms that functionalization gave peak changes of M-O, M-OH,–OH, C-O, and C=C. XRD characterization indicates the ZnFe2O4 structure for the calcined Zn-Fe-LDH. EDS confirms content of Fe (29.5 %w), Zn (7.7%w), O (18.2%w). SEM characterization indicated that ZnFe2O4/AC composite has irregular shape particle with some holes on its surface. Adsorption test confirms that ZnFe2O4/AC composite gave adsorption percentage of paracetamol about 4 times larger than wood char, 2.8 times larger than activated carbon, and 1.5 times larger than Zn-Fe-LDH/AC composite. Adsorption capacity of paracetamol by ZnFe2O4/AC is 7.36 mg/g (Langmuir model) and 5.63 mg/g (Dubinin Radushkevic model). Adsorption energy is 223.61 J/mol, indicating the physical adsorption mechanism.

Keywords: *composite, wood char, functionalization, adsorption*

1. INTRODUCTION

Wood is one of lognocellulosic material, i.e a material which is rich of cellulose, lignin, and hemicellulose [1]. This material can be conversed to char or called as biochar by thermal [2] or hydrothermal pyrolysis process [3] . In Indonesian society, the wood char is usually used as fuel for cooking of roasted fishes, chicken, and meats. This char can be used as adsorbent but really needs to improve its characteristics, especially its porosity because its process does not involve any activation treatment. The char activation can use various activator, including bases such as

KOH and NaOH [4] acids, such as H3PO4 [5], and salts, such as various metal chlorides, including ZnCl2, CoCl2, NiCl2, CuCl2, FeCl3, and CrCl3 [6]. KOH is one of base activators which successfully produced the activated carbon from rice huskwith large surface area (2201 m2/g) and improves its performance in adsorption of Na+ [7]. The other research reported that KOH activation in activated carbon preparation from giant knotweed Reynoutria sachalinensis gives the best surface area of 2541 m2/g [8]

Oxidation treatment of activated carbon is a method to improve polar oxygenated functional groups of the carbon surface. Some oxidators can be used in this treatment, including single acids such as HNO3, H2O2, and H2SO4 [9], double acids such as H2SO4-HNO3, H3PO4-HNO3, H2O2–HNO3) [10], or various salt, such as KMnO4, K2S2O8, K2Cr2O7 [11]. Oxidation of activated carbon using HNO3 at 60oC improves –COOH groups on carbon surface and adsorption of Pb(II),

Cu(II), and Ni(II) [12]. Functionalization using H2SO4 at 80oC (13) and 100oC [14] produce the sulphonated carbon which improves catalytic reaction.

Modification of biochar using Mg-Al-LDH and Mg-Fe-LDH can increase adsorption of phosphate [15]. Zn-Fe-LDH has been formed by coprecipitaion of Zn(II) and Fe(III) nitrate solution using NaOH solution. Calcination of LDH not only changes hydroxide to oxide, but also removal of anion by thermal decomposition reaction Calcination of Zn-Fe-LDH forms ZnFe-LDO or ZnFe2O4 [16]. The ZnFe-LDO/AC composite from wood char showed good adsorption of paracetamol. The wood char was activated by KOH and oxidized by H2SO4 before modification with Zn-Fe-LDO [17]. Layered double hydroxide or LDH is hidroxyde substance which has chemical formula of [M(II)1–xM(III)x(OH)2] (An–)x/n . mH2O. LDH is class of substance in which chemical structure as same as brucite [18]. The divalent cations, such as Zn2+ or Ni2 , Ca2+, Co2+, Cu2+ and trivalent metal cations, such as Al3+, Cr3+, Fe3+, occupy in octahedral centres and hydroxide ions form dimension 2 layers. Water molecules and anions, such as CO32−, NO3−, Cl−, SO42− , PO43-, stay in each space between layers [19].

In this research, wood char was activated using KOH activator, oxidized using HNO3, and modified using Zn-Fe-LDH and Zn-Fe-LDO for adsorption of paracetamol. This organic substance is one medicines which is potential as pollutant in water environment.

2. METHODOLOGY

2.1. Activation of wood char

A 1 kg of wood char was crushed and sieved to get the char particle size of 30 -60 mesh. The prepared wood char (10 g) was mixed with 120 mL of KOH solution (4M,) and shaked for 2 h at room temperature. The residue of decantation was dried at 105oC and calcined at 500oC for 5 minutes to produce the activated carbon. After washing the carbon using HCl solution (1M), the product was dried at 105oC for 6 h.

2.2. Preparation of ZnFe-LDH/AC and Zn-Fe-LDO/AC

This procedures referes the previous research [17] by some differences. The actived carbon was oxidized using HNO3 solution (6 M) at ratio of 1:10 (g/mL) by heating at 80 oC for 3 h. The product was washed by destilated water and dried at 70 oC for 1 night. The 0.5 g of actived carbon was mixed with FeCl3 and ZnCl2 solutions in Zn(II)/Fe(III) mol ratio of 5:1. and shaked at 175 rpm for 1 h, then precipited with NaOH solution (5 M) at pH condition of 7 under stirring. Then, the suspension was heated at 80oC for 3 h. The mixture was filtered, washed, dried at 70 oC for 24 h to form ZnFe-LDH/AC, and finally calcined to 950 oC for 10 minutes to get ZnFe2O4/AC or Zn-Fe-LDO/AC composite.

For comparation of phase in characterization with X-ray diffraction, ZnO/AC and Fe2O3/AC were also synthesized by applying the same procedure, except without FeCl3 and ZnCl2, respectively.

2.3 Adsorption test of paracetamol

Each wood char, the activated carbon, Zn-Fe-LDH/AC, and ZnFe2O4/AC (0.1 g) and paracetamol solution (100 mg/L ; 25 mL) were mixed and shaked at 200 rpm for 24 h. After filtration, paracetamol concentration was analyzed by UV-Vis spectrophotometry analysis. The procedures were repeated in 3 times. The best adsorbent (ZnFe2O4/AC) was used to determine adsorption capacity by adsorption in the same way but in concentration range of 10 – 100 mg/L.

3. RESULT AND DISCUSSION

3.1. Functional groups of the products

Changing of the carbon functional groups was identified using FTIR spectrophotometry and reported in Figure 1. The wood char before treatment shows weak FTIR spectra of functional groups, including C=O (1700 cm-1), C=C (1600 cm-1), and C-O (1200 cm-1). No bands at 2900 cm-1 , connected to aliphatic hydrocarbon. It indicates that the wood was pyrolized well in wood char production. Activation of the wood char using KOH caused weaker bands of FTIR spectra which indicates more pyrolysis reaction along activation process.

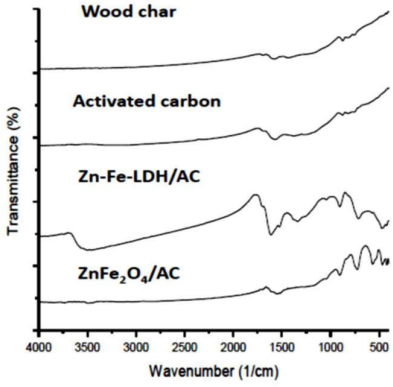

Figure 1. FTIR spectra of wood char before and after treatment by KOH activation and modification with Zn-Fe-LDH/AC and ZnFe2O4/AC

Modification of the activated carbon with Zn-Fe-LDH gives changing of the activated carbon spectra pattern, i.e. sharper spectra at about 1600 cm-1, 1350 cm-1, and 460 cm-1. Based on Balcolm et al [20], bands at about 460 cm-1 is connected to vibration of M-O-H and at 1350 cm-1 is connected to carbonate anions in LDH structure. The carbonate anion may be from dissolved or adsorbed CO2 (by the carbon) and reacts with H2O molecules to form H2CO3.

Band at 1600 cm-1 is related to bending vibration of H2O. The Zn-Fe-LDH/AC composite shows sharper band of -OH at wavenumbers of 3500 and1600 cm-1 which shows increasing of H2O and –OH in Zn-Fe-LDH. Bands at 800 and 700 cm-1 are related to M-O vibration. Calcination of Zn-Fe-LDH/AC remove some bands which indicates dehydration, dehydroxilation, and carbonate decomposition reactions.

3.2. Crystal structure of composite

Characterization using X-ray diffraction has been conducted to identify phase and crystal structure of the synthesized ZnFe2O4/AC (Zn-Fe-LDO/AC). The synthesized product was presented in Figure 2 and interpreted in Table 1 using the synthesized ZnO/AC and ZnFe2O4 from reference.

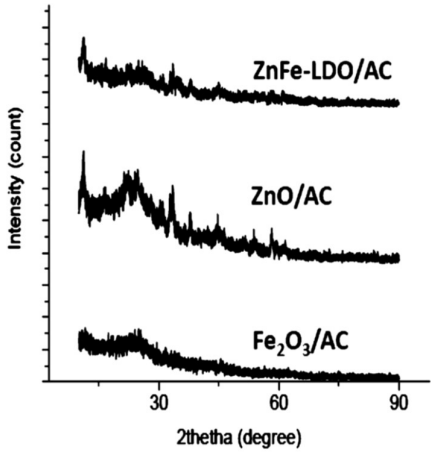

Figure 2. X-ray diffractogram of ZnFe2O4/AC, ZnO/AC, and Fe2O3/AC from wood char using KOH activator and HNO3 oxidator.

Figure 2 shows that all diffractograms show wide peaks. They indicate amorph phase of biochar. However, both composites of Zn-Fe-LDO/AC and ZnO/AC also show some sharp peaks.

It indicates the crystal phases. The diffractogram data of both composites in Table 1 indicates that sample of ZnFe2O4/AC also contains ZnO. It may be because amount of ZnCl2 is higher than FeCl3 so that some of ZnCl2 reacted with some gases which were emitted by decomposition of biochar in calcination process to form ZnO.

Table 1. Diffractogram data ofsSynthetized ZnFe2O4/AC, synthetized ZnO/AC, and ZnFe2O4 from reference

Synthetized $ZnFe_2O_4$/AC			Synthetized ZnO/AC			$ZnFe_2O_4$ [21]	
2Θ	d-spacing	I_R	2Θ	d-pacing	I_R	d-spacing	(hkl)
11.24	7.88	100	11.14	7.94	100		
22.43	3.96	19	22.22	4.00	22		
32.93	2.72	40	32.83	2.73	61	2,97	22
33.55	2.67	59	33.45	2.68	72		
37.94	2.37	37	37.84	2.38	33		
44.81	2.02	18	44.62	2.03	14	2.10	400
58.35	1.58	24	58.17	1.59	32	1.50	440

3.3. Composition and morphology of composites

The composite which has been synthesized at Fe(III)/Zn(II) mol ratio of 1:5 was characterized using SEM-EDS. Result of analysis, including SEM image, EDX-graph, and EDX table, are shown in Figure 3. Based on the data in EDX table, the graph in Figure 4 is formed. The graph in Figure 4 shows that amount of Zn2+ component is dominant in the composite. Lower amount of C element may be caused by decomposition of biochar in calcination process. Existence of Cl element is from chloride salts. Based on structure of LDH, the Cl- anions occupy the space between each 2 layers.

Morphology of composite was characterized by SEM at some different magnification (Figure 3). The SEM images show irregular morphologies with some holes and white spots, indicating oxide metals.

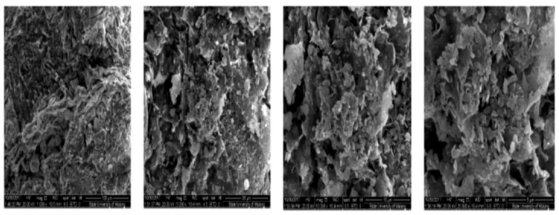

Figure 3. SEM images of the synthesized ZnFe2O4/AC

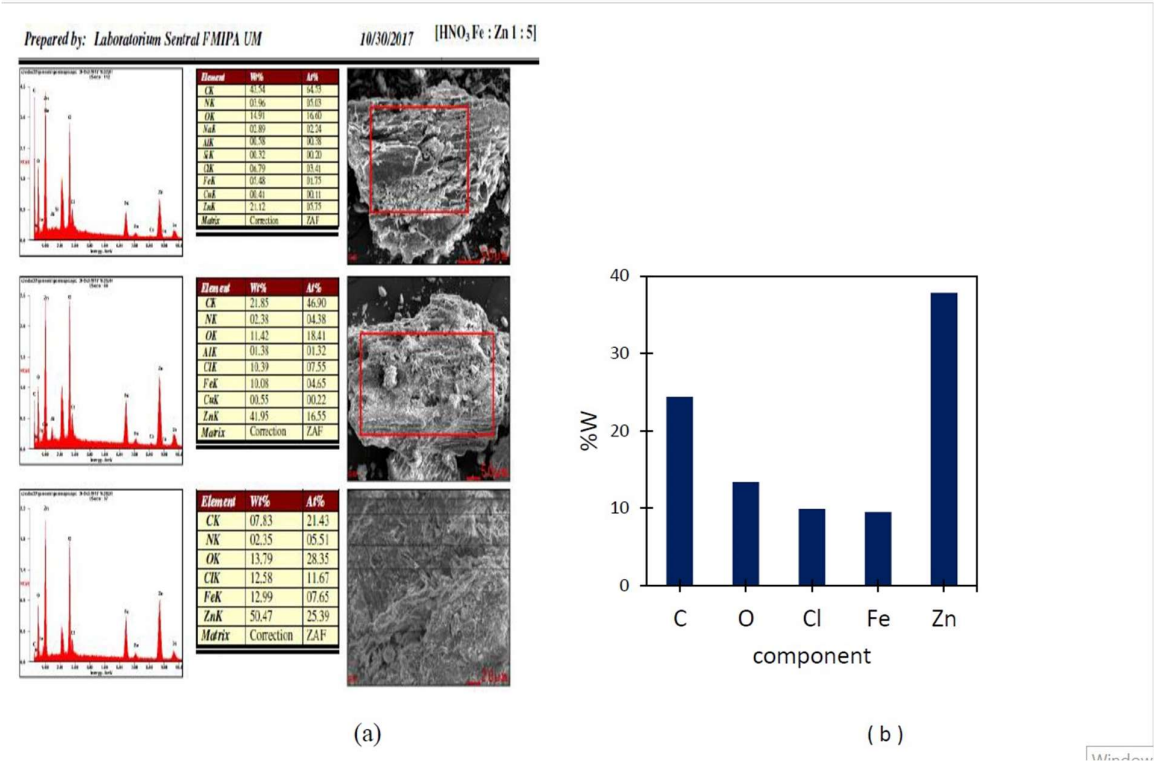

Figure 4. a) Spectra, data and SEM image of ZnFe2O4/AC composite identified using SEM-EDS, b) graph of the composite's components

3.4. Adsorption test

Adsorption test of paracetamol by the wood char before and after functionalization (activation and modification) was showed in Figure 5.

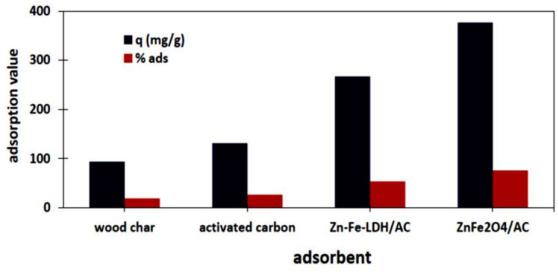

Figure 5. Adsorption of paracetamol using wood char and functionalized wood char

Figure 5 shows that adsorption by the activated carbon is 1.4 times larger than wood char. It may be due to improvement of porosity by activation reaction. Modification of the activated carbon using Zn-Fe-LDH causes adsorption is 2.8 times larger than wood char. It is because existence of Lewis acids such as Fe(III) and Zn(II) in the LDH structure improve affinity of adsorbent toward polar functional groups of adsorbate (paracetamol). Besides that, hydroxides in LDH structure also play the same role.

Modification of the activated carbon with ZnFe2O4 as composite of ZnFe2O4/AC increases adsorption 4 times larger than the wood char. The calcination process has changed the LDH to LDO. Those structures are different related to removal of anions and dehydration of the LDH. Based on existence of hydrodes on the surface of the LDH, the reaction causes decreasing of polarity, but the calcination increases the spaces between layers of LDH due to removal of some chloride and H2O. This case probably causes improvement of adsorption of paracetamol.

3.5 Adsorption Capacity

Adsorption at various paracetamol concentrations has been conducted to build isotherm curves (Figure 6) based on 3 different isotherm models, including Langmuir, Freundlich, and Dubinin –Radushkevic (DR). All isotherm curves show correlation coefisients > 0.95. It indicates that all adsorption isotherms are fit with those all models, so that all those models can be used to determine adsorption parameters. Some calculated adsorption parameters are listed in Table 2. Data in Table 2 shows that monolayer adsorption capacity is 7.37 mg/g (Langmuir) and 6.54 mg/g (DR).

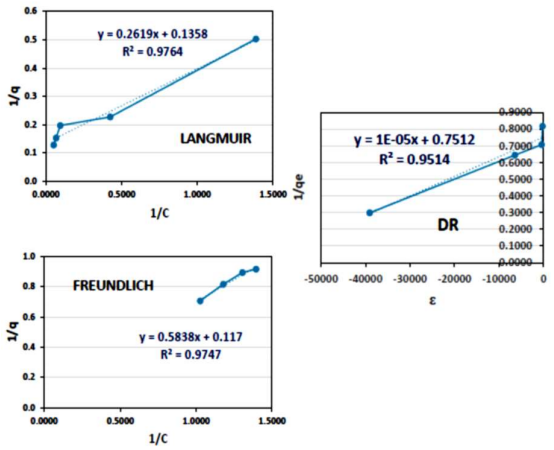

Figure 6. Adsorption isotherms of paracetamol by the composite of ZnFe2O4/AC using 3 different models

Adsorption energy can be used to predict adsorption mechanism. The adsorption energy < 8 KJ/mol indicates physical adsorption mechanism, in other side in the range of 8-16 KJ/mol indicates chemical adsorption mechanism [22]. From this research, the calculated adsorption energy is 223,61 J/mol which indicates that paracetamol adsorption process through physical mechanism.

Freundlich constant, i.e n, is indicator of adsorption intensity. The n range of 1 - 10 describes beneficial/favorable adsorption [23]. The n value which can be achieved from this research is 1.71. It indicates that adsorption of paracetamol by ZnFe2O4/AC is favorable.

Table 2. Adsorption parameter based on 3 different isotherm models

Parameter	Nilai	Satuan
Langmuir :		
q_m	7.36	mg/g
K_L	0.52	
R^2	0.98	
Dubinin – Raduskevich :		
q_s	5.64	mg/g
K_{DR}	0.00001	
E	223.61	J/mol
R^2	0.95	
Freundlich :		
K_F	1.31	mL/g
n	1.71	
R^2	0.97	

4. CONCLUSION

Functionalization of wood char has been performed, including activation, oxidation, and modification. Characterization using FTIR spectrophotometry shows that functionalization causes changing of functional groups, especialy –OH, C=O, C-O, and M-O. X-ray diffraction characterization indicates that composite consists of ZnFe2O4, ZnO, and amorphous biochar structure. SEM – EDS characterization identifies component of Zn, Fe, C, and O.

Modification of wood char as Zn-Fe-LDO/AC increases adsorption 1.5 times larger than Zn-Fe-LDH/AC, 2.8 times larger than activated carbon, and 4 times larger than wood char.

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