Effect of metal cation ratio on chemical properties of ZnFe$_2$O$_4$/AC composite and adsorption of organic contaminant

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Abstract. Porous woody char is biochar prepared through pyrolysis. The biochar can be used as adsorbent. In this research, ZnFe$_2$O$_4$/AC composite was synthesized through impregnation of the woody biochar with ZnFe$_2$O$_4$ to study effect of mol ratio of Fe(III) and Zn(II) toward their physicochemistry and adsorption of drug wastewater. Paracetamol was used as adsorbate model. This research was conducted in several steps, including activation of the woody biochar using KOH activator at temperatur 500 °C for 15 min to produce the activated carbon, functionalization of the carbon using H$_2$SO$_4$ oxidator (6M) at temperature of 80 °C for 3 h, impregnation of the oxidized activated carbon with Zn-Fe-LDH (Layered Double Hydroxide) at various mol ratio of Fe(III) and Zn(II), including 1:2, 1:3 and 1:4 using NaOH solution (5M) for coprecipitation, and calcination of Zn-Fe-LDH/AC at 950 °C for 5 min to produce ZnFe$_2$O$_4$/AC. FTIR diffraction characterization indicated existence of M-O (M=Zn(II), Fe(III)) and OH functional groups. FTIR spectra showed increasing of bands connected to –OH by increasing of the ratio till the ratio was achieved at 1:4, then decreased again. The ratio mol showed effect on the adsorption of paracetamol. Profile of adsorption value was fit with changing of functional groups. The highest adsorption was achieved at the ratio of 1:4. After calcination it gave the adsorption value of 17.66 mg/g.

Key words: activated carbon, ZnFe$_2$O$_4$, Zn-Fe-LDH, adsorption

1. Introduction
Pharmacy industry is one of industries which produce dangerous wastewater for ecosystem, derived from production process, washing process, laboratory activity, and remain product due to failure of production process. The wastewater can be overcame by adsorption method carbon as adsorbent. Adsorption method is more advantageous than other methods due to economical, efficient, and easily applied [1].

Adsorption is a process in which atoms, ions, or molecules from substances such as gas, liquid, or solublle solid are concentrated on porous surface of an adsorbent [2]. There are various adsorbents, such as alumina, zeolite, activated carbon, biomass, polymers, and silica gel [3]. Activated carbon adsorbent has been applied and developed, due to its characteristics such as not poisonous, abundant, economical, and biodegradable. Activated carbon is the best adsorbent in adsorption system because it has large surface area and high adsorption performance so that its usage can be optimal [4]. Surface area of activated carbon is about 300 – 3000 m$^2$/g. Activated carbon can be made from animal bones or plant biomass such as wood, rice husk, corn cob, coconut shell, hard wood, and coal [5].

Paracetamol is one of medicinal wastewater components. Activated carbon has been applied in adsorption of paracetamol and showed good performance [6]. Development of many researchs have been conducted to improve performance of activated carbon as adsorbent. One of the is modification of activated carbon with metal chloride salts such as ZnCl$_2$ and FeCl$_3$ [7] or ZnO and Fe$_2$O$_3$ as product of calcination [8]. Fe (III) and Zn (II) have different charges so that they have different affinities toward polar organic substances in adsorption process. So that, this research is focussed on studying of Fe(III)/Zn(II) mol ratio influence on paracetamol adsorption.
2. Experiment

2.1. Preparation of activated carbon from wood char
Wood char from market (1 kg) was crushed and conditioned to obtain particle size of 30–60 mesh. Mixture of KOH solution (4M, 100 mL) and wood char (10 g) was shaken for 2 h at room temperature. After decantation, the residue was dried at 105°C and calcined at 500°C for 10 minutes. The product was washed with HCl solution (1M) and aquadest, then it was dried at 105°C for 6 h.

2.2. Functionalization of activated carbon by oxidation
The activated carbon was suspended in H₂SO₄ solution (6 M) at the carbon and solution ratio of 1:10 (g/mL) and heated at 800°C for 3 h. The product was washed by aquadest and dried at 70°C for 1 h.

2.3. Preparation of composites
This procedure is combination of procedures applied in previous researches [9, 10]. The activated carbon (0.5 g), FeCl₃ and ZnCl₂ solutions (each 0.2M and 50 mL) were mixed and shaken at 175 rpm for 1 h, then dropped with NaOH solution (5 M) under stirring to achieve pH of 7 condition. The synthesis was conducted at the Zn(II)/Fe(III) ratio of 1:2 to 1:4. Then, the mixture was heated at 80°C for 3 h. The mixture was filtered, washed, dried at 70°C for 24 h, and finally calcined to 950°C for 5 minutes to get ZnFe₂O₄/AC composite. The same procedure was applied without FeCl₃ solution to produce ZnO/AC and without ZnCl₂ solution to produce Fe₂O₃/AC.

2.4 Adsorption test
The prepared composites (0.1 g) and paracetamol solution (100 mg/L ; 25 mL) were mixed and shaken at 200 rpm for 24 h. After filtration, paracetamol concentration was analyzed by UV-Vis spectrophotometry analysis. The procedures were conducted in 3 times of repetition.

3. Results and Discussions

3.1. Functional group characterization by FTIR spectrophotometry

![Figure 1. FTIR spectra of ZnFe₂O₄ composite at various Fe(III) and Zn(II) mol ratio](image)

Characterization of the products by FTIR spectrophotometry was conducted to identify the change of wavelength shift and sharpness of bands of the composites’ spectra, as shown at Figure 1. FTIR spectra in Figure 1 shows that no significant wavelength difference of the composite spectra at various Fe(III) and Zn(II) ratio. Spectra of ZnFe₂O₄/AC has bands at 3000-3500 cm⁻¹, connected to hydroxyl group (vO-H). The spectra bands at 903.39; 905.31; and 905.31 cm⁻¹ indicate presence of Cl⁻ ion. The bands at range of 400-900 cm⁻¹ are connected to Fe(III) – O and Zn(II) – O. However, the cation ratio gives significant effect on intensity of the spectra. Intensities of the
bands at range of 400-900 cm\(^{-1}\) were increased by increasing of Zn(II)/Fe(III) ratio from 1:2 to 1:4 due to improvement of metal content in the composite [11]. Besides that, band of hydroxil was also increased by increasing of the ratio which indicates increasing of hydroxil functional groups connected to phenolic groups on graphene layers of the activated carbon in the composite.

3.2. Characterization of crystal structure by XRD method

Characterization by XRD has been conducted to identify chemical structure of the composites. Figure 2 shows that the diffractogram of ZnFe\(_2\)O\(_4\)/AC composite contains of diffractogram peaks of the synthesized ZnO/AC and the synthesized Fe\(_2\)O\(_3\)/AC which indicates that the ZnFe\(_2\)O\(_4\)/AC composite also contains both structures.

![Figure 2. X-ray diffractogram of the synthesized ZnFe\(_2\)O\(_4\)/AC, ZnO/AC, and Fe\(_2\)O\(_3\)/AC](image)

| Table 1. Interpretation of the ZnFe\(_2\)O\(_4\)/AC, ZnO/AC, and Fe\(_2\)O\(_3\)/AC composite diffractograms |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Synthesized ZnFe\(_2\)O\(_4\)/AC composite at 1:4 ratio | Synthesized ZnO/AC | Synthesized Fe\(_2\)O\(_3\)/AC | Synthesized ZnFe\(_2\)O\(_4\) |
| Zn(II)/Fe(III) | 2\(\theta\) | d (Å) | I\(_R\) (%) | 2\(\theta\) | d (Å) | I\(_R\) (%) | 2\(\theta\) | d (Å) | I\(_R\) (%) | d-spacing (Å) |
| ZnFe\(_2\)O\(_4\)/AC 1:4 | 11.16 | 7.93 | 100.0 | 11.09 | 7.97 | 100.00 | - | - | - | - |
| ZnO/AC | 22.43 | 3.96 | 23.32 | 22.22 | 4.00 | 27.00 | - | - | - | - |
| Fe\(_2\)O\(_3\)/AC | 24.86 | 3.58 | 15.97 | 24.78 | 3.59 | 32.59 | - | - | - | - |
| ZnFe\(_2\)O\(_4\) | 31.70 | 2.82 | 94.01 | - | - | - | 31,66 | 2.82 | 100.0 | 2.97 (220) |
| ZnO/AC | 32.89 | 2.72 | 43.47 | 32.80 | 2.73 | 65.19 | - | - | - | - |
| Fe\(_2\)O\(_3\)/AC | 33.58 | 2.67 | 69.44 | 33.45 | 2.68 | 79.31 | - | - | - | 2.53 (311) |
| ZnFe\(_2\)O\(_4\) | 45.42 | 1.99 | 61.91 | - | - | - | 45,41 | 1.99 | 61.91 | 2.10 (400) |
| ZnO/AC | 51.33 | 1.78 | 10.29 | 51,31 | 1.78 | 8.39 | - | - | - | 1.71 (422) |
| Fe\(_2\)O\(_3\)/AC | 56.47 | 1.63 | 12.10 | - | - | - | 56,46 | 1.63 | 17.18 | 1.61 (511) |
| ZnFe\(_2\)O\(_4\) | 58.34 | 1.58 | 26.96 | 58.20 | 1.58 | 33.11 | - | - | - | 1.50 (440) |
| ZnO/AC | 83.93 | 1.15 | 7.42 | - | - | - | - | - | - | 1.15 | 5.34 | - |

As interpreted in Table 1, the d-spacing data of the synthesized ZnFe\(_2\)O\(_4\)/AC diffractogram is fit with d-spacing data of the ZnFe\(_2\)O\(_4\)/AC diffractogram from the previous research [12]. It indicates that the synthesized composite at the 1:4 ratio contains ZnFe\(_2\)O\(_4\) structure.

3.3. Adsorption test

Adsorption test has been performed and the data of adsorption was reported in Figure 3.
Figure 3 shows increasing of adsorption by increasing of the Zn(II)/Fe(III) ratio. It is due to increasing of Lewis acid such as Zn(II) cations in the composites which improve affinity of the composite toward Lewis bases paracetamol structure such as O atoms at –OH and C=O groups and N atom at –NH group.

4. Conclusion
ZnFe$_2$O$_4$/AC has been synthesized at various cation ratios of Zn(II)/Fe(III). Characterization by FTIR spectrophotometry indicates increasing of hydroxil and metal oxide contents by increasing of the cation ratio. Characterization by XRD indicates presence of ZnFe$_2$O$_4$, ZnO, and Fe$_2$O$_3$ in the composite. Adsorption test shows improvement of adsorption by improvement of the cation ratio.

Reference
[1] Oktem, Y.A. et al 2008 Bioresource Technology 99 (5) pp.1089-1096.
[2] Liu, Y., Y. Zheng, dan A. Wang. 2009 Journal of Environmental Sciences 22(4) pp 486-493
[3] Tripathi, A. dan M. R. Ranjan 2015 Bioremed Biodeg 6 p315
[4] Prabowo, A.L. 2009 Pembuatan Karbon Aktif dari Tongkol Jagung serta Aplikasinya untuk Adsorpsi Cu, Pb, dan Amonia Depok Universitas Indonesia
[5] Sembiring, T.M dan T.S Sinaga 2003 Arang Aktif (Pengenalan dan Proses Pembuatannya), Universitas Sumatera Utara, Medan.
[6] Dutta, M., Das, U., Mondal, S., Bhattachriya, S., Khatun, R., dan Bagal, R. 2015 International Journal of Environmental Sciences 6(2) pp 270-281
[7] Park, S.J., Jang, Y.S., Shim, J.W., Ryu, S.K. 2003 Journal of Colloid and Interface Science 260 pp 259–264
[8] Pereira, M.F.R., Soares, S.F., Órfão, J.J.M., Figueiredo, J.L. 2003 Carbon 41 pp 811–821
[9] Hongo, Teruhisa., Takeshi Iemura, and Atsushi Yamazaki 2008 Journal of the Ceramic Society of Japan 116 pp 192-197
[10] Ahmed, A.A.A., Talib, Z.A., Hussein, M.Z., Flaifel, M.H., and Al-Hada, N.M., 2014 Journal of Spectroscopy 2014 Article ID 732163, 6 pages.
[11] Wan, J., Jiang, X., Li, H., and Chen, K. 2012 Journal of Material Chemistry 22 pp 13500-13505.
[12] Lemine, O.M., Bououdina, M., Sajieddine, A.M. Al-Saie., Shafi, A., Khatab, M., Al-Hilali, and Henini. 2011 *Physica B* 406 pp 1989-1994