

Effect of metal cation ratio on chemical properties of ZnFe₂O₄/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, ZnFe₂O₄/AC composite was synthesized through impregnation of the woody biochar with ZnFe₂O₄ 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 temperature 500 °C for 15 min to produce the activated carbon, functionalization of the carbon using H₂SO₄ 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 ZnFe₂O₄/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, ZnFe₂O₄, 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 overcome 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 soluble 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 m²/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 researches have been conducted to improve performance of activated carbon as adsorbent. One of them is modification of activated carbon with metal chloride salts such as ZnCl₂ and FeCl₃ [7] or ZnO and Fe₂O₃ 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. Functionalitaton of actived carbon by oxidation

The activated carbon was suspended in H_2SO_4 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 procedures is combination of procedures applied in previous researchs [9, 10]. The activated carbon (0.5 g), FeCl_3 and ZnCl_2 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 $\text{ZnFe}_2\text{O}_4/\text{AC}$ composite. The same procedure was applied without FeCl_3 solution to produce ZnO/AC and without ZnCl_2 solution to produce $\text{Fe}_2\text{O}_3/\text{AC}$.

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

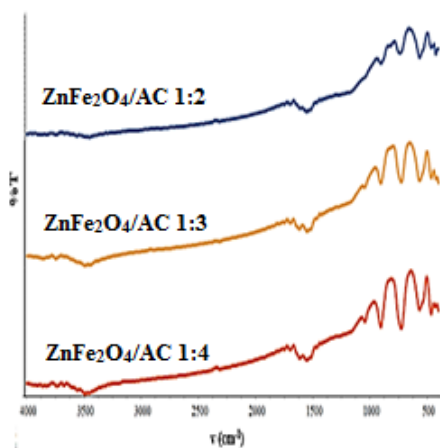


Figure 1. FTIR spectra of ZnFe_2O_4 composite at various Fe(III) and Zn(II) mol ratio

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 $\text{ZnFe}_2\text{O}_4/\text{AC}$ has bands at 3000-3500 cm^{-1} , connected to hydroxyl group ($\nu_{\text{O-H}}$). 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 $400\text{--}900\text{ cm}^{-1}$ 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 hydroxyl was also increased by increasing of the ratio which indicates increasing of hydroxyl 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 $\text{ZnFe}_2\text{O}_4/\text{AC}$ composite contains of diffractogram peaks of the synthesized ZnO/AC and the synthesized $\text{Fe}_2\text{O}_3/\text{AC}$ which indicates that the $\text{ZnFe}_2\text{O}_4/\text{AC}$ composite also contains both structures.

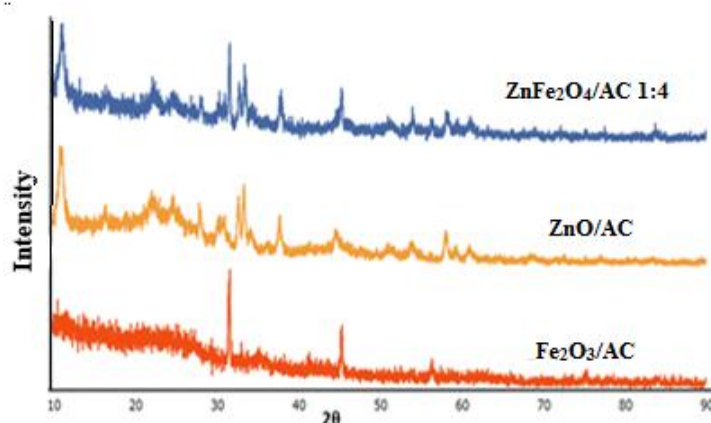


Figure 2. X-ray diffractogram of the synthesized $\text{ZnFe}_2\text{O}_4/\text{AC}$, ZnO/AC , and $\text{Fe}_2\text{O}_3/\text{AC}$

Table 1. Interpretation of the $\text{ZnFe}_2\text{O}_4/\text{AC}$, ZnO/AC , and $\text{Fe}_2\text{O}_3/\text{AC}$ composite diffractograms

Synthesized $\text{ZnFe}_2\text{O}_4/\text{AC}$ composite at 1:4 ratio Zn(II)/Fe(III)			Synthesized ZnO/AC			Synthesized $\text{Fe}_2\text{O}_3/\text{AC}$			ZnFe_2O_4 [12]
2θ	d (Å)	I_R (%)	2θ	d (Å)	I_R (%)	2θ	d (Å)	I_R (%)	d-spacing (Å)
11,16	7,93	100,0	11,09	7,97	100,00	-	-	-	-
22,43	3,96	23,32	22,22	4,00	27,00	-	-	-	-
24,86	3,58	15,97	24,78	3,59	32,59	-	-	-	-
31,70	2,82	94,01	-	-	-	31,66	2,82	100,0	2,97 (220)
32,89	2,72	43,47	32,80	2,73	65,19	-	-	-	-
33,58	2,67	69,44	33,45	2,68	79,31	-	-	-	2,53 (311)
45,42	1,99	61,91	-	-	-	45,41	1,99	61,91	2,10 (400)
51,33	1,78	10,29	51,31	1,78	8,39	-	-	-	1,71 (422)
56,47	1,63	12,10	-	-	-	56,46	1,63	17,18	1,61 (511)
58,34	1,58	26,96	58,20	1,58	33,11	-	-	-	1,50 (440)
83,93	1,15	7,42	-	-	-	-	1,15	5,34	-

As interpreted in Table 1, the d-spacing data of the synthesized $\text{ZnFe}_2\text{O}_4/\text{AC}$ diffractogram is fit with d-spacing data of the $\text{ZnFe}_2\text{O}_4/\text{AC}$ diffractogram from the previous research [12]. It indicates that the synthesized composite at the 1:4 ratio contains ZnFe_2O_4 structure.

3.3. Adsorption test

Adsorption test has been performed and the data of adsorption was reported in Figure 3.

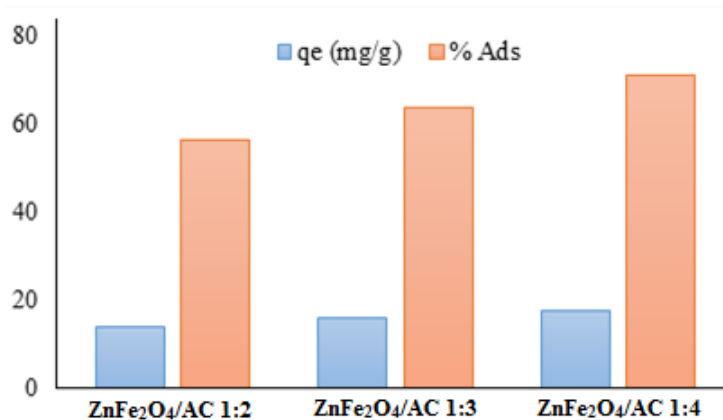


Figure 3. Adsorption values of paracetamol by ZnFe₂O₄/AC composite

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

ZnFe₂O₄/AC has been synthesized at various cation ratios of Zn(II)/Fe(III). Characterization by FTIR spectrophotometry indicates increasing of hydroxyl and metal oxide contents by increasing of the cation ratio. Characterization by XRD indicates presence of ZnFe₂O₄, ZnO, and Fe₂O₃ in the composite. Adsorption test shows improvement of adsorption by improvement of the cation ratio.

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