STUDY OF SALT OXIDATOR TYPE INFLUENCE ON PHYSICOCHEMISTRY OF PATCHOULI BIOCHAR – Cr_2O_3 COMPOSITE AND ORGANIC CONTAMINANT ADSORPTION

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ABSTRACT

Organic wastewater, including drug wastewater, creates serious problems in life due to its risks, such as drug retention and toxicity for both human or animals. Biochar is a porous material which can be used as adsorbent for wastewater remediation. Formation of composite by impregnating the biochar with metal oxides can improve performance of biochar in adsorption. Oxidation of biochar surface before the impregnation was studied in this research. Purpose of this research is to study its effect on its characteristics and adsorption of paracetamol, as the contaminant model. Synthesis was conducted in some steps, including preparation of the activated biochar from patchouli biomass through pyrolysis at 450°C using ZnCl_2 activator, functionalization of biochar using 3 different salts (KMnO_4 , $\text{K}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{Cr}_2\text{O}_7$) at 60°C , impregnation of the activated biochar using CrCl_3 0.9 M, and calcination of the biochar- CrCl_3 composite to form biochar- Cr_2O_3 composite at 600°C . Adsorption test used paracetamol (100 ppm) as pollutant model with batch method (175 rpm, 24 h). X-ray diffraction characterization indicated impregnant structure of Cr_2O_3 . Characterization using FTIR spectrophotometry showed different patterns, especially connected to C=O and OH bands by using oxidators in sequence of $\text{K}_2\text{S}_2\text{O}_8 > \text{KMnO}_4 > \text{K}_2\text{Cr}_2\text{O}_7$. SEM-EDX characterization showed different content of Cr(III) in the composites prepared in oxidator sequence of $\text{K}_2\text{Cr}_2\text{O}_7 > \text{K}_2\text{S}_2\text{O}_8 > \text{KMnO}_4$. SEM images of the composites indicated the irregular ball shapes. Adsorption values were obtained more in same sequence of oxidator type based on FTIR spectrophotometry characterization than SEM-EDX.

Keywords: salt oxidator, composite, patchouli, adsorption, physicochemistry

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1. INTRODUCTION

Biochar is a porous carbaceous material. This material can be prepared by pyrolysis of various biomass such as wood, manure, industrial sludge, and agriculture residues [1,2]. Porous characteristics of biochar causes biochar can be applied for adsorption of various adsorbates, including various heavy metal cations [3, 4, 5, 6], anions [3, 6, 7, 8], and organic adsorbates [9, 10, 11]. Chemical properties of biochar can be improved to increase performance of biochar as adsorbent, i.e by combining it using various metal oxides to form a composite [12, 13, 14] or by functionalizing it using various oxidators to improve acid functional groups on its surface [15, 16, 17, 18].

Type of oxidator gave effect on type of surface functional groups on carbaceous materials. For example, peroxide acid oxidation improved the functional groups such as C=O, C-O, and OH on biochar [19]. HNO₃ oxidation can increase the –NO₂, C=O, and COOH functional groups. HNO₃-H₂SO₄ mixture increased the –NO(OH), and NH₃ – Na₂S₂O₄ mixture improves the –NH₂ [17]. Functionalization of activated carbon using concentrated H₂SO₄ dan CH₃COOH improves carboxyl groups on its surface [16, Anjum 2016]. Oxidation of activated carbon using concentrated HNO₃ increased carboxyl [15, 16]. Functionalization of carbon using concentrated H₂SO₄ produced sulphonated carbon [20, 21].

Beside type of oxidator, the other parameter such as time and calcination treatment also influence the surface functional group of biochar. For example, too long oxidation process decreased acid functional groups of biochar [16]. Increasing of calcination temperature decreased the carboxyl and phenolic groups of biochar and no acidity after calcination at 950 °C. [22]. Porosity of biochar was also influenced by oxidation. For example both micropore and mesopore were formed by using each HNO₃, H₂SO₄, H₂O₂ and KMnO₄ in oxidation of biochar [23].

Oxidation of biochar can improve or reduce organic substance adsorption. It really depends on polarity of adsorbate. For example, at pH 2, oxidation of norit carbon using HNO₃ increased adsorption of aniline but reduced adsorption of nitrobenzene [22].

Oxidation of biochar surface can improve metal cation adsorption by biochar [24, 15]. Impregnant on biochar using metal oxide is started with oxidation of biochar surface before impregnation to improve impregnant amount, such as with acids [24,25]. In this research, biochar was oxidized using 3 different salts (KMnO₄, K₂S₂O₈, and K₂Cr₂O₇). Purpose of this research is to study effect of salt type on the composite's surface functional groups and adsorption of contaminant model, paracetamol.

2. MATERIALS & EXPERIMENTAL PROCEDURES

2.1. Materials

This research used some chemicals, including KMnO₄ (Merck), K₂S₂O₈ (Merck), and K₂Cr₂O₇ (Merck), CrCl₃.6H₂O (Merck), ZnCl₂ (Merck), paracetamol (pharmacy), destilated water.

2.2. Methods

2.2.1. Preparation of biochar using ZnCl_2 activator

A mixture was prepared, consisted by patchouli biomass (60 g), ZnCl_2 (180 g) and destilated water (360 mL) were mixed and evaporated at 100 °C, then pyrolyzed to 450 °C for 0.5 h in the closed porcelain cup. Due to the cup size, the ZnCl_2 impregnated biomass was divided to become 3 parts. The calcined composite product was washed using HCl solution (1M) and destilated water to remove the activator. The product was dried at 130 °C for 6 h.

2.2.2. Oxidation of biochar surface

Biochar (5 g) was mixed with salt solution (100 mL, 5 %) and heated to 60 °C for 0.5 h. The product was then washed using destilated water and dried at 100 °C for 6 h.

2.2.3. Impregnation of the oxidized biochar

The oxidized biochar (0.7 g) was mixed with CrCl_3 solution (0.9 M, 100 mL) and shaken at 200 rpm for 24 h. The filtrate was removed by decantation. Then, the impregnated biochar was calcined at 600 °C for 1 h to produce biochar – Cr_2O_3 composite.

2.2.4. Characterization of the composite

FTIR spectrophotometer (Shimadzu) was used to characterize functional groups of the products with Pellet kalium bromide (KBr) technique. The dried biochars was mixed with the oven-dried KBr (Merck).

X-ray powder diffraction (XRD) was used to characterize crystal structure of the composite. Data of the X-ray diffractometer was collected in 2θ range of 10–90° with Cu metal target ($K_\alpha = 1.54 \text{ \AA}$) at the instrument condition of 30 mA, 40 kV, and receiving slit size of 0.1 mm.

Surface Area Analyzer (SAA) was used to measure nitrogen gas adsorption and desorption for determination porosity of the composite. The composites were outgassed at 300 °C for 3 h before adsorption. The adsorption process was conducted at 77.5 K.

Scanning Electron Microscope (SEM) was used to characterize morphology of the composite and Energy Dispersive X-ray (EDX) was used to characterize component of the composite.

2.2.5. Adsorption Test

Paracetamol solution (100 ppm, 25 mL) was mixed with each the composites (0.05 g) and shaken at 175 rpm for 24 h. The mixtures were filtered and the filtrates were analyzed using UV–Vis spectrophotometry at maximum wavelength (243 nm). Standart curve of paracetamol was made based on measurement of a paracetamol solution serie at 10 – 50 ppm. Concentration data of paracetamol before (C_o) and after (C_t) adsorption process was used to calculate adsorption percentage as follows:

$$\% \text{ adsorption} = \frac{C_o - C_t}{C_o} \times 100\%$$

3. RESULTS AND DISCUSSIONS

3.1. Characterization of the composites using FTIR spectrophotometry

Identification of the composites' surface functional groups has been conducted using FTIR spectrophotometry. The FTIR spectra is shown in Figure 1 and Figure 3.

Figure 1. FTIR spectra of patchouli biochar oxidized 3 different oxidator salts

Figure 1 shows spectra in which the bands connected to OH, C=O and C-OH at 3415, 1620 and 1020 cm⁻¹, respectively. The C=O bands of the biochars oxidized using the oxidators are sharper bands than the one which was not oxidized. It indicates that there is improvement of the functional group content. The OH band at about 3415 cm⁻¹ indicates the hydroxyl or hydrate. By referring to interpretation given by the previous research [26], the C=O functional group in range of 1600 – 1650 cm⁻¹ is connected to C=O of quinone, carbonyl, and carboxyl. Improvement of both bands in around 3400 and 1020 cm⁻¹ indicates the carboxyl group, because band at 1020 cm⁻¹ indicates C-OH functional group. Increasing of those functional groups may be connected to oxidation-reduction reaction between surface of biochar and the oxidators.

Based on some considerations as follows : a) biochar contains the layered aromatics 2D structures like graphite [27], oxidation reaction of the graphite with oxidator KMnO₄ and H₂Cr₂O₄ produced functional groups of C=O and COOH [28], c) oxidation of CNT by KMnO₄ produced hydroxyl groups [29], and d) FTIR spectra of the oxidized biochar in this research which indicates C=O, OH, and C-OH functional groups, so that oxidation reaction is proposed in Figure 2.

Figure 2. Prediction of acid functional groups formation on layer of biochar by oxidation reaction based on FTIR spectra of biochar

Figure 3 shows spectra of the biochar-Cr₂O₃ composite after calcination. Compared to Figure 2, the spectra in Figure 3 show the reduced bands which indicated the thermal reaction

which decomposed the OH functional groups. By referring to the previous research [30] the sharp double bands between 500 and 600 cm^{-1} indicate Cr-O band of Cr_2O_3 .

Figure 3. FTIR spectra of composites 300 using 3 different oxidator mixture

3.2. Characterization of the Composites using X-ray diffraction

The impregnant of biochar, CrCl_3 , has potency to react with oxide gases in calcination process to form metal oxide. The oxide gases may be emitted by thermal degradation reaction of biochar surface. In this subsection, result of characterization of the composite using X-ray diffraction method is reported. Purpose of this characterization is to identify crystal structure of impregnant in the composite. X-ray diffractogram of the composite prepared using oxidator of KMnO_4 is presented in Figure 4 and interpretation of the diffractogram is listed in Table 1.

Figure 4 showed some peaks which indicated that the composite contains crystal structure. By comparing diffractogram data of Cr_2O_3 in previous research [30,32] the composite indicated that it contained Cr_2O_3 structure.

Figure 4. X-ray diffractogram of biochar – Cr_2O_3 composite prepared using oxidator of KMnO_4

Table 1. X-ray diffractogram data of biochar – Cr₂O₃ composite prepared using oxidator of KMnO₄ and Cr₂O₃ structure as comparison

Sampel			Cr ₂ O ₃ [32,33]		
2θ	d (Å)	I _R (%)	2θ	d(Å)	hkl
24.3	3.66	100	24.52	3.63	012
33.48	2.68	14.67	33.62	2.66	104
35.99	2.50	25.09	36.25	2.47	110
54.64	1.68	17.21	54.89	1.67	116
64.93	1.43	7.33	65.19	1.43	214

3.3. Characterization of Composte's Content Using EDX

Figure 5. EDX graphs of the biochar – Cr₂O₃ composites prepared using K₂Cr₂O₇ oxidator

Component of composite has been analysed quantitatively using EDX. The EDX graphs were reported in Figure 5 - 7 and average Cr component in the composites was described in Figure 8. The average components were calculated from 2 nearest data of EDX in Figure 5 - 7. The oxidators showed different effect on the composition of composite. The bochar surface which was oxidized using KMnO₄ shows mol amount of C is about 3 times than Cr, whereas the

biochar which was oxidized using $K_2Cr_2O_7$ shows more Cr than C and the biochar which was oxidized using $K_2S_2O_8$ has similar amount between Cr and C. This composition may be influenced by different strength of oxidators. Reduction potential data of the oxidators increases by sequence of $KMnO_4$ (+0.56) < $K_2Cr_2O_7$ (+1.33) < $K_2S_2O_8$ (+2.11) [33]. It means that strength of oxidator has sequence of $K_2S_2O_8$ > $K_2Cr_2O_7$ > $KMnO_4$. The mol amount of C atom in the composite decreases by increasing of those oxidators' strength due to thermal decomposition of biochar in the composite caused by oxidation action by the oxidators.

The mol amount of Cr increases from usage of $KMnO_4$ to usage of $K_2Cr_2O_7$. It may be connected to sharper C=O and –OH bands so that it increases affinity of biochar toward Cr(III) in impregnation process. However, usage of $K_2S_2O_8$ have caused decreasing again mol amount of Cr, compared to usage of $K_2Cr_2O_7$. It may be connected to decreasing amount of C atom which indicates less biochar which causes less porosity and surface area which reduces contact place of $CrCl_3$ on biochar surface in impregnation adsorption.

3.4. Characterization of the Composite's Morphology using SEM

Figure 6. EDX graphs of the composites prepared using $K_2S_2O_8$ oxidator

Morphology of the composites has been characterized using SEM to study effect of oxidator type toward morphology of the composite. The result of the characterization was reported in Figure 7. SEM images in Figure 9 shows that the composite prepared using oxidator of $KMnO_4$

shows ball shape. Increasing of oxidator strength ($\text{KMnO}_4 < \text{K}_2\text{Cr}_2\text{O}_7 < \text{K}_2\text{S}_2\text{O}_8$) indicates the increasing damage of the shape.

3.5 Adsorption Test of the Composite

The composite was tested in adsorption of a contaminant model, i.e paracetamol. Result of the application test was shown in Figure 8. Figure 10 shows that usage of $\text{K}_2\text{S}_2\text{O}_8$ oxidator gave the highest adsorption value. Connected to Figure 7, it indicates that morphology of the composite doesn't give effect on the adsorption. Related to Figure 6, the O and Cr amount factor seems to influence adsorption. $\text{K}_2\text{S}_2\text{O}_8$ oxidator causes formation of the composite which has most amount of Cr(III) and more oxy functional groups than usage of $\text{K}_2\text{Cr}_2\text{O}_7$. Those both factors seems responsible toward the highest adsorption. Usage of KMnO_4 causes higher adsorption than $\text{K}_2\text{Cr}_2\text{O}_7$. It may be because amount of O in the composite prepared using the former is almost 2 times higher than usage of the later. The O amount indicates acid oxy functional groups of biochar surface.

Figure 7. EDX graphs of the composites prepared using KMnO_4 oxidator

Figure 8. Component of the composites prepared using 3 different oxidators: A (KMnO_4), B ($\text{K}_2\text{Cr}_2\text{O}_7$), C ($\text{K}_2\text{S}_2\text{O}_8$), identified using EDX

Figure 9. SEM images of the composites prepared using 3 different oxidator salts

Figure 10 Adsorption of paracetamol (100 ppm) by composites prepared using 3 different oxidators :
A). KMnO₄, B) K₂Cr₂O₇, C) K₂S₂O₈

4. CONCLUSION

Synthesis, characterization, and application of biochar – Cr₂O₃ composites have been studied. Based on this research, some conclusions can be taken. First. Oxidator salt type have influence on functional groups of the composite surface, surface morphology, and adsorption of paracetamol. Best morphology was achieved by usage of KMnO₄, but the highest content of – OH was indicated by usage of K₂S₂O₈ as well as the highest adsorption.

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Composite and Organic Contaminant Adsorption

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