

Preparation and Characterization of Composite from Poly(vinyl chloride) Hydrochar and Hydrolyzate of Keratin from Chicken Feather by Hydrothermal Carbonization

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Received: 28 June 2021;

Accepted: 16 August 2021;

Published online: 20 September 2021;

AJC-20524

Poly(vinyl chloride) and chicken feather wastes considered as the dangerous wastes. This study aimed to characterize the prepared composite from poly(vinyl chloride) hydrochar and keratin hydrolyzate from chicken feather to get possibility the usage of this composite as soil amendment. The poly(vinyl chloride) hydrochar-keratin hydrolyzate composites (HKHC) had been produced with the hydrothermal carbonization process. The composites were made from different composition of poly(vinyl chloride):chicken feather (5:95% (HKHC5), 10:90% (HKHC10) and 15:85% (HKHC15)). The hydrothermal carbonization process would break and fracture the CHCl bond of poly(vinyl chloride). Moreover, this process would also hydrolyze keratin from chicken feather into small protein. The composite structure was formed from aromatic carbon and amino acids aggregate along with other organic substances. The solid composites and liquid residues formed in this process. The composites were characterized by FTIR, XRD and TEM and the composite of char-Fe₃O₄ was characterized by SEM. Meanwhile, the liquid residues were analyzed for its organochlorine by GC-MS and amino acid contents by HPLC. The results showed that all products have similar properties but the composite with ratio 5:95% (HKHC5) had the highest aromatic structure, paramagnetic (Fe₃O₄) crystallinity and amino acid contents.

Keywords: Composite, Poly(vinyl chloride), Chicken feather, Hydrothermal carbonization.

INTRODUCTION

Among all the waste materials, plastic waste has been an environmental concern. Due to its non-degradable nature, plastic considerably harms living beings. The most commonly used plastic is polyvinyl chloride (PVC) [1], due to the presence of basic building block of chlorine, it is nearly non-degradable. PVC disposal through incineration should be avoided because it leads to the production of toxic organochlorine gases such as polychlorinated dibenzofuran (PCDF) and polychlorinated dibenzodioxin (PCDD) [2]. The same result occurs through pyrolysis, which leads to the release of chlorophenol, polyaromatic hydrocarbons, PCDD, chlorobenzene and PCDF [3], which are toxic organochlorine compounds. However, PVC decomposition using hydrothermal carbonization (HTC) does not generate PCDF, PCDD or other organochlorine gases. Chlorine gas is transformed into chlorinated hydrocarbons and hydrochloric acid at trace levels [4]. Additive base compounds, for example, Na₂CO₃ are added to increase PVC dechlorination efficiency in hydrothermal carbonization [5].

In the poultry industry, chicken feathers are generated as the waste products. This industry annually faces a serious waste problem. Globally, > 4 × 10⁶ tonnes of chicken feathers are produced annually as waste [6] and this number may increase with increase in population. The traditional approaches to poultry waste disposal include burial in landfills, burning or using the waste as livestock feed. However, these methods are not environmentally friendly because greenhouse gases are produced during these processes [7]. Since chicken feathers comprise 90% keratin [8], they require long time period to decompose in soil. Keratin is pliable, durable, chemically unreactive and insoluble in organic solvents [9]. The use of chicken feathers as a raw material to prepare hydrolyzate is a novel approach to poultry waste disposal. Keratin or hydrolyzate is formed using chicken feathers by hydrolyzing or processing them with hydrothermal carbonization. This method has a carbon efficiency of approximately 100%; thus, it is safe [10].

PVC and Fe₃O₄ composites were synthesized as adsorbents through hydrothermal carbonization [11]. Hydrochar gene-

rated exhibited a high Fe_3O_4 content and large homogenous surface. The C-Cl bonds remained in hydrochar. Biomass, *i.e.*, chicken feather, and additive bases, including Na_2CO_3 , are required to completely eliminate organic chloride bonds [4,5]. Materials comprising paramagnetic substances, in combination with organic materials, can be employed as precursors to prepare soil amendment. Soil amendment includes numerous humus materials. PVC and chicken feather hydrochar-keratin hydrolyzate composite (HKHC) are considered soil amendment agents, which may serve in rapid synthesis of humus like materials. Humus formation or humification can naturally occur, but it requires a long time. Naturally, humus is formed from the decomposition of living organisms, which are chemically and biologically transformed into soil to aggregate several compounds that can interact through hydrogen bonds [12]. Soil humus constitutes heterogeneous aromatic and aliphatic and hydrophobic molecules. The humic molecules are arranged in supramolecular structures stabilized with hydrophobic non-covalent bonds [13]. This study synthesized organic hydrochar by using chicken feathers and PVC as main materials through hydrothermal carbonization.

EXPERIMENTAL

The main materials employed were chicken feathers and poly(vinyl chloride) (PVC) obtained from Ar-Royan Chicken Slaughter house, Yogyakarta and E-Merck, respectively. The remaining chemicals were *n*-hexane, anhydrous sodium sulphate, sodium carbonate and dichloromethane obtained from Merck and iron(II/III) oxide purchased from Aldrich, USA.

Synthesis of composites: The different ratios of PVC and chicken feathers *viz.* 10:90 (HKHC10), 5:95 (HKHC5) and 15:85 (HKHC15) were used for the synthesis of composites. In a beaker glass comprising 700 mL of distilled water, 300 g of chicken feather and PVC was added. For HKHC5, 15 g of each sodium carbonate and Fe_3O_4 was added to the mixture. For HKHC10 and HKHC15, 30 and 45 g, respectively, of each sodium carbonate and Fe_3O_4 were added. In a, hydrothermal carbonization (HTC) reactor, the mixture was introduced. HTC was heated for 3 h at 160-170 °C and 9-10 atm pressure. The solid product of HTC was filtered and dried for 24 h in an oven at 100 °C. The liquid residue of HTC was characterized.

Synthesis of char- Fe_3O_4 composite: Fe_3O_4 (5 g), PVC (5 g) and sodium carbonate (5 g) were added to a glass beaker with 500 mL of distilled water. Using 2 M sulphuric acid, the mixture acidity was set to pH 6. Then, the mixture was placed into the hydrothermal carbonization (HTC) reactor and performed at 185 ± 5 °C. The char slurry was filtered and then washed with 100 mL of distilled and double distilled water. In oven, the composite was dried for 24 h at 100 °C. This char- Fe_3O_4 composite was analyzed through scanning electron microscopy (SEM, JSM-6510LA).

Organochlorine analysis: In this experiment, the method given in APHA [14] was followed. Using Whatman filter paper (90 mm), 100 mL of all liquid residues was filtered to eliminate suspended materials. The resulting solution was poured in a 500 mL separating funnel. A mixture of *n*-hexane (12.5 mL) and dichloromethane (12.5 mL) (1:1) was added to the separ-

ating funnel and was rapidly shaken for 2 min until two layers were formed. Aqueous and organic layers were collected in different beaker glasses. Using 6.25 mL of same solution, the aqueous layer was re-extracted twice. The acquired organic layers were collected in the same beaker and then were poured in a glass funnel comprising 2.5 g of anhydrous sodium sulphate. This extract was concentrated to 2 mL by using a rotary evaporator and was injected in a GC-MS system.

Determination of nitrogen total by Kjeldahl method:

Nitrogen concentrations of liquid and solid HKHC products were determined. Each sample (0.2 g) was placed in a Kjeldahl flask. Subsequently, conc. H_2SO_4 (4 mL) and the N catalyst (0.7 g) were added. Wet destruction was conducted until the solution colour changed to green. Afterwards, the samples were cooled down. The samples were then diluted using 10 mL of distilled water. Before distillation, dilute NaOH (20 mL) was added to the sample and the distillate was collected in an Erlenmeyer flask comprising 4 drops of BCG-MR indicator and H_3BO_3 (4%). Distillation was performed until the distillate volume was 60 mL. The colour turned to blue from red. The distillate was titrated against 0.02 N HCl until the colour changed to red from blue. The volume of HCl was utilized to estimate the nitrogen concentration using the following formula:

$$\text{N (\%)} = \frac{\text{Titration volume (mL)} \times \text{Normalize HCl (0.02 N)} \times \text{Nitrogen atom mass (14.008)}}{\text{Sample mass (mg)}} \times 100$$

$$\text{Protein concentration (\%)} = \text{Nitrogen concentration (\%)} \times \text{Conversion factor (6.25)}$$

Amino acid determination: Composite (60 mg) and liquid residue (60 mg) were mixed with 4 mL of 6 N HCl. The mixture was heated at 110 °C for 24 h and then cooled to room temperature. Mixture pH was adjusted to 7 with 6 N NaOH. To a mixture, distilled water was added to obtain 10 mL volume. The mixture (50 μL) was added to a vial with 300 μL of *ortho*-phthalaldehyde. This vial was shaken for 5 min and then, 10 μL of the sample was injected into the HPLC system.

Characterization of composites: The functional groups of main materials and each composite were estimated through FTIR (Shimadzu Prestige-21). In composites, the presence of chloride and iron was determined through X-ray diffraction (XRD, Shimadzu-6000) with $\text{CuK}\alpha$ radiation.

GC-MS (QP2010S Shimadzu) with helium as the carrier gas and a flame thermionic detector was employed to confirm the absence of organochlorine compounds. The column, Rtx 5, with the flow rate of 0.50 mL/min was used. The injection and column temperatures were 300 and 70 °C, respectively.

Transmission electron microscopy (TEM, JEOL-JEM 1400) was used to investigate the size and shape of composites. In liquid residue and composite, the amino acid content was estimated using high-performance liquid chromatography (HPLC, Thermo ultimate-3000) having a fluorescence detector. LiChrospher 100 RP-18 (5 μm) was used as the column at the flow rate of 1.5 mL/min. The mobile phase comprised: phases A (CH_3OH :50 mM sodium acetate:THF (2:96:2) pH 6.8) and B (65% CH_3OH).

RESULTS AND DISCUSSION

FTIR studies: The IR absorption spectra of pure PVC, chicken feathers and the three composites confirmed the success of hydrothermal carbonization (HTC) process (Fig. 1). The absorption bands of PVC included C-Cl of CHCl (690 cm^{-1}) and C-H of CHCl (1252 and 1329 cm^{-1}) [15]. These peaks were not observed in the absorption spectra of HKHC10, HKHC5 and HKHC15 because during HTC, the CHCl bonds of PVC broke. Hence, the composite products did not exhibit compounds with C-Cl bonds. Absorption bands at 555 cm^{-1} obtained for HKHC10, HKHC5 and HKHC15 indicated the presence of Fe-O groups in Fe_3O_4 . In chicken feather keratin, disulphide bonds appeared at 617 cm^{-1} . This absorption band was not obtained for the composite spectrum because disulphide bonds, whose decomposition was difficult in chicken feathers, were broken and turned into degradable proteins. However, -SH group absorption was not observed in the composite spectra, which indicated that disulphide bond decomposition leads to SO_4^{2-} formation in the liquid residue and not -SH group generation. In keratin, the absorption band appearing at 1118 cm^{-1} indicated the existence of C-O ester and this band disappeared after HTC process.

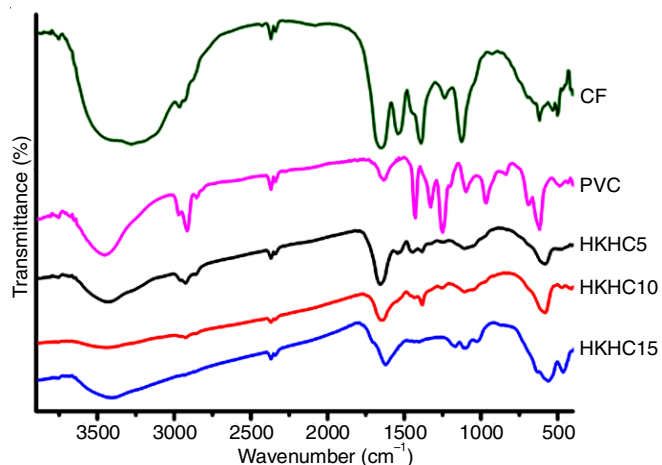


Fig. 1. FTIR spectra of PVC, chicken feather (CF), HKHC5, HKHC10 and HKHC15

For chicken feather spectra, bands at 1545 and 1387 cm^{-1} were associated with keratin amide groups, *i.e.* N-H and C-N bonds, respectively [16]. These two bands were also observed in the FTIR spectra HKHC10, HKHC5 and HKHC15 in a small intensity because of keratin hydrolysis to amino acids. The peak for C=O bond was observed near 1637 cm^{-1} , which weakened after HTC because of decarboxylation [17]. In HKHC10, HKHC5 and HKHC15 spectra, this peak was observed as the aromatic C=C vibrations [5] and overlapped with C=O vibrations. The existence of aromatic structure revealed that three composites exhibited properties similar to humus and thus could be utilised as the soil amendment. HKHC5 exhibited the highest peak at 1637 cm^{-1} , among the three composites, indicating the optimum aromatic structure. The broad band obtained at 3430 cm^{-1} represented the existence of O-H and N-H in carboxyl and amino acids, respectively.

XRD studies: Fig. 2 shows the XRD patterns of HKHC10, HKHC5, HKHC15, NaCl and pure Fe_3O_4 . The XRD patterns of three composites were compared with those of NaCl and pure Fe_3O_4 . For Fe_3O_4 powder, five intensive peaks appeared at the 2θ of 35.5° , 62.7° , 57.1° , 30.2° and 43.2° . Three composites exhibited the same intensive peaks due to Fe_3O_4 . The Fe_3O_4 peak intensity increased after HTC, revealing that Fe_3O_4 crystallinity was higher in composites than in the Fe_3O_4 . Among all the three composites, HKHC5 exhibited the maximum Fe_3O_4 crystallinity. As humus, these composites showed paramagnetic properties because of magnetite contents [18].

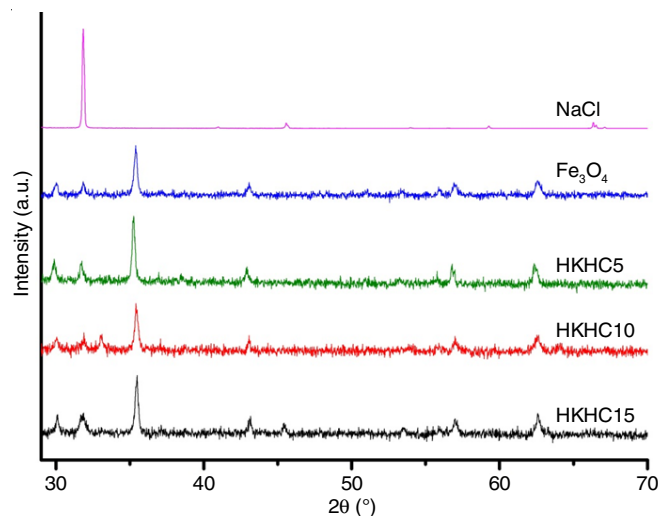


Fig. 2. Diffractograms of pure NaCl, Fe_3O_4 , HKHC5, HKHC10 and HKHC15

Moreover, among the three composites, HKHC15, exhibited the same peaks as NaCl appearing at 2θ of 31.8° , 45.5° , and 66.3° . NaCl was formed towards the end of the reaction. PVC was dechlorinated because of heat during HTC. Sodium cations of Na_2CO_3 (additive base) attracted Cl^- anions in the redox reaction. The XRD patterns of HKHC15 showed strong NaCl peaks, suggesting that the redox reaction enhances when in the presence of Na_2CO_3 and PVC in HTC. In HTC, HKHC15 serves optimally in PVC dechlorination.

SEM studies: Char- Fe_3O_4 SEM images revealed the Fe_3O_4 position in PVC char. Fine-pollen-like particles were present on round char (Fig. 3). These particles were interpreted as Fe_3O_4 . Char- Fe_3O_4 SEM images indicated the possibility of Fe_3O_4 dispersion on the char surface during HTC. Char- Fe_3O_4 particles tend to spread than HKHC composite.

TEM studies: From TEM images, different PVC concentrations led to different polyaromatic layer forms but similar paramagnetic particle shapes (Fig. 4). Paramagnetic particles were coated with a keratin polyaromatic layer, which rendered particle agglomeration in the centre. The dark and light sides of TEM images showed the presence of Fe_3O_4 particles and polyaromatic compounds, respectively. In HKHC5, Fe_3O_4 particles had a large size because they were highly agglomerated with keratin addition. However, in HKHC15, the same particles exhibited a small size because PVC addition caused the paramagnetic layers to spread instead of agglomerate. During HTC

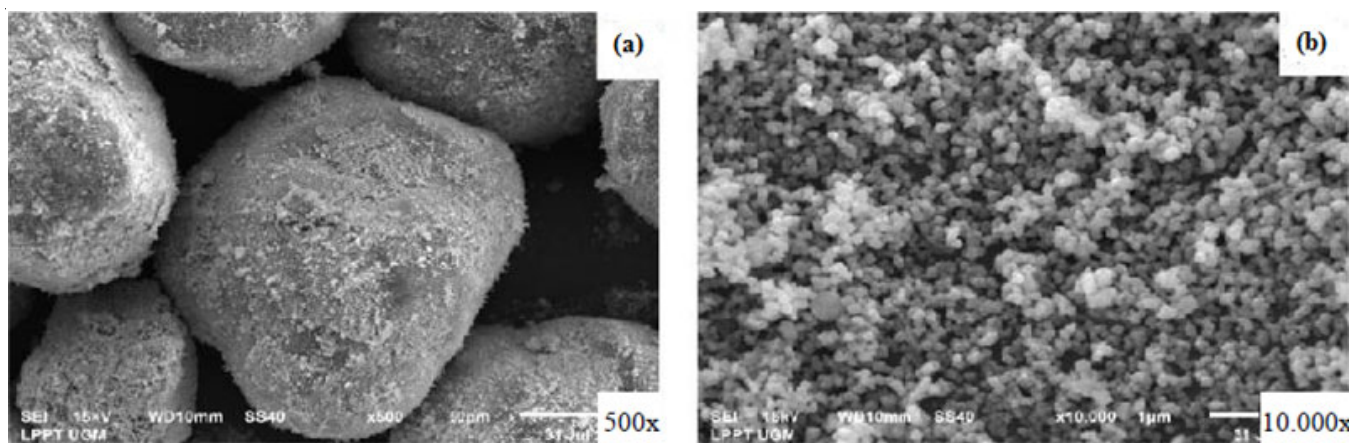


Fig. 3. SEM images of char-Fe₃O₄ at 50 μm (a) and 1 μm (b)

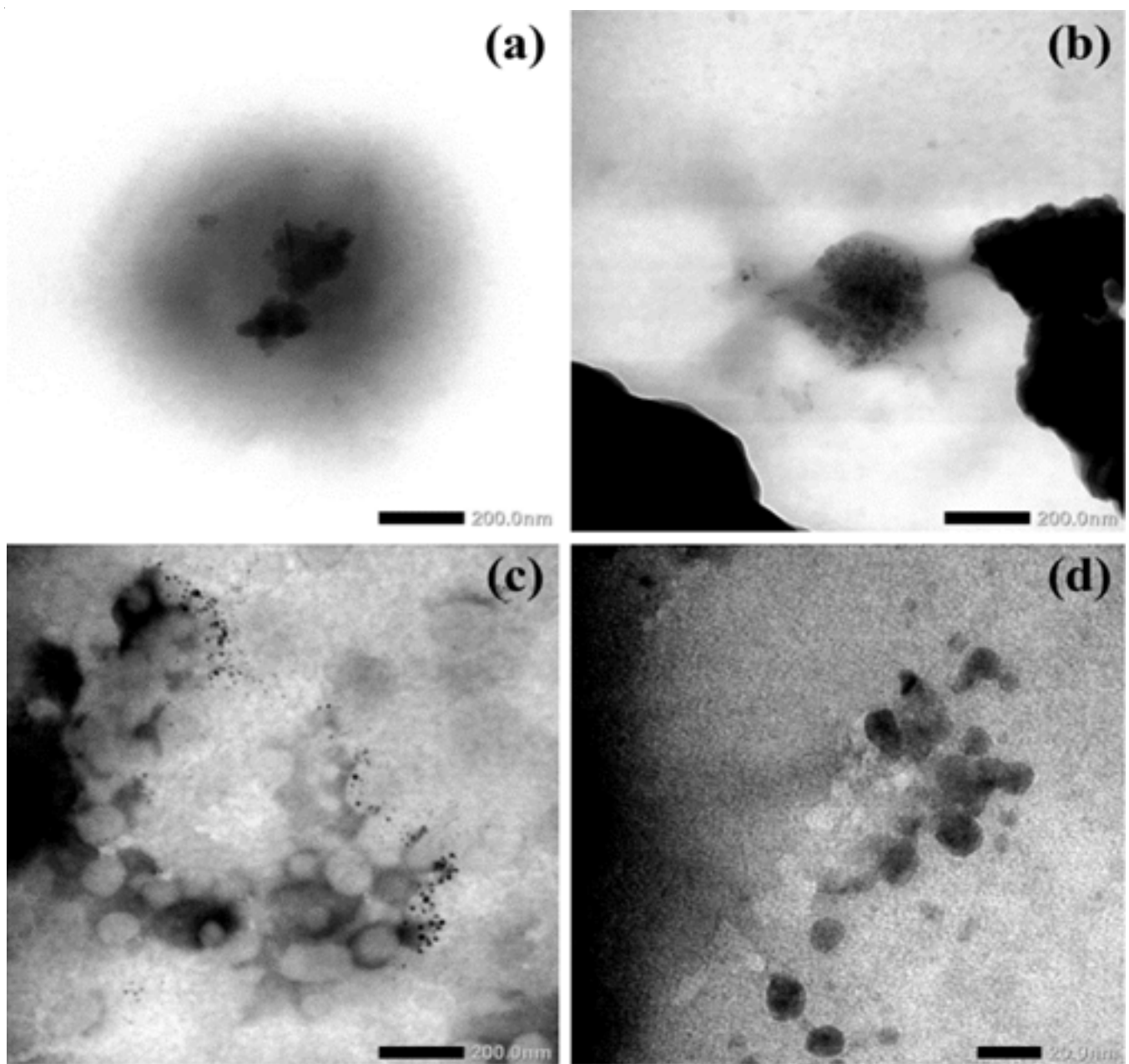


Fig. 4. TEM images of HKHC5 at 200 nm (a), HKHC10 at 200 nm (b), HKHC15 at 200 nm (c) and HKHC15 at 20 nm (d)

process, PVC structures fractured and disintegrated into porous materials because of volatile gas released (Fig. 4c-d) [5]. Thus, HKHC15 was the most effective composite for PVC dechlorination. These particle size of ≥ 20 nm exhibited superparamagnetic properties [9] (Fig. 4d).

Determination of organochlorine in liquid residue of composites: Organochlorine present in the liquid residue was determined to analyze the composite quality as the soil amendment. For its use as the soil amendment, composites must contain no toxic organochlorine compounds. For qualitative analyses of organochlorine, GC-MS with the flame thermionic detector was employed. Before instrumental analyses, from the liquid residues of the three composites, organochlorine compounds were extracted. No chromatogram showed any peak in 0-60 min, indicating that liquid residues of any composite did not comprise organochlorine (Fig. 5). HTC successfully removed all organochlorine traces from the composites. In PVC, Cl was transformed into various harmless compounds, including NaCl and HCl [19]. This result is confirmed with XRD spectra. Therefore, these three composites could be utilized as harmless soil amendments.

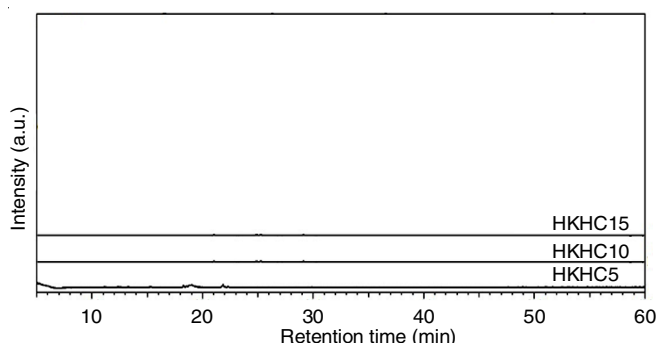


Fig. 5. Chromatogram of HKHC5, HKHC10 and HKHC15

Determination of nitrogen and amino acids in composites: In three composites and their liquid residues, nitrogen present was determined using the Kjeldahl method (Table-1). In chicken feather, amino acids are obtained from keratin hydrolyzate. The total concentrations of amino acids and nitrogen were equal to the chicken feather mass employed to fabricate composite. HKHC5, with the highest keratin percentage, showed the maximum nitrogen percentage. HKHC5 comprised 27.67% chicken feathers. Thus, in HKHC5, nitrogen and keratin were 3.98% and 24.9%, respectively. These results were obtained using the Kjeldahl method for the three composites. In HKHC5, total nitrogen was 4.75%; thus, total protein was 29.68%. Tables 2 and 3 showed the profiles of amino acids in the liquid residue and composite.

TABLE-1
TOTAL NITROGEN CONCENTRATION
IN HKHC5, HKHC10 AND HKHC15

Sample	Nitrogen concentration (%)		
	HKHC5	HKHC10	HKHC15
Solid composite	2.60	1.79	1.41
Liquid residue	2.15	1.51	1.43
Total	4.75	3.30	2.84

TABLE-2
AMINO ACIDS PRESENT IN HKHC5, HKHC10 AND HKHC15

Amino acid	HKHC5 (%)	HKHC10 (%)	HKHC15 (%)
Aspartic acid	0.07	0.07	0.14
Glutamic acid	0.64	1.04	1.00
Serine	0.03	0.11	0.02
Threonine	0.58	1.93	0.75
Alanine	0.05	0.37	0.00
Tyrosine	0.62	0.96	0.93
Methionine	0.27	0.37	0.62
Valine	0.23	0.76	0.19
Phenylalanine	0.57	0.72	0.75
Isoleucine	0.25	0.42	0.36
Leucine	0.33	0.45	0.41
Lysine	0.43	0.60	0.57
Total	4.07	6.80	5.74

TABLE-3
AMINO ACIDS PRESENT IN LIQUID RESIDUE
OF HKHC5, HKHC10 AND HKHC15

Amino acid	HKHC5 (%)	HKHC10 (%)	HKHC15 (%)
Aspartic acid	0.24	0.26	0.30
Glutamic acid	1.92	1.36	1.45
Serine	0.26	0.10	0.05
Threonine	2.71	1.78	1.68
Alanine	0.44	0.07	0.00
Tyrosine	1.92	1.40	1.46
Methionine	0.29	0.25	0.36
Valine	1.24	0.44	0.26
Phenylalanine	1.53	1.36	1.27
Isoleucine	0.53	0.37	0.36
Leucine	0.91	0.78	0.66
Lysine	1.01	0.83	0.76
Total	12.99	9.00	8.61

To calculate the percentage and determine the type of all amino acids, the liquid residue and composite were analyzed using HPLC. The HKHC5 liquid residue exhibited the highest amino acid percentage of 12.99%. In HKHC10 and HKHC5 composites and liquid residues, 12 amino acids were detected, whereas in HKHC15, only 11 amino acids were present, which indicated that HKHC5 and HKHC10 provided better hydrolysis than HKHC15.

In the liquid residues and composites, cysteine amino acid was not present because oxygen-containing compounds react with the -SH group of cysteine and form water soluble SO_2 , which turns into SO_4^{2-} ; thus, SO_4^{2-} was absent in the solid composite. Another reason may be that sulphur, which in keratin, generates the most amino acids, and in the liquid residue, reacts with H to produce H_2S gas. Hence, amino acids, including methionine or cysteine, are absent or available in low concentrations. The liquid residues have abundant organic compounds, such as amino acid [20]; thus, they can be utilized as liquid soil amendments.

Conclusion

The keratin hydrolyzate and PVC HKHC were fabricated by through hydrothermal carbonization process. The FTIR results revealed the appearance of new peaks in the fabricated composites. Of the three composites, HKHC5 exhibited the optimum aromatic structure. In its liquid residue, HKHC5

showed the highest amino acid content and Fe₃O₄ crystallinity. Thus, HKHC5 was the optimum composite for use as soil amendment. The other two composites can also be utilized as soil amendment since they contain no organochlorines and have properties similar to humus. Therefore, HKHC5 can be used effectively for PVC dechlorination.

ACKNOWLEDGEMENTS

This publication was supported by the PPUPT Project of Universitas Gadjah Mada, by No. of Contract of 1929/UNI/DITLIT/DIT-LIT/PT/2020.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. C.J. Rhodes, *Sci. Progr.*, **101**, 207 (2018); <https://doi.org/10.3184/003685018X15294876706211>
2. M. Picone, E. Delaney, D. Tagliapietra, I. Guarneri and A.V. Ghirardini, *Front. Ecol. Evol.*, **8**, 235 (2020); <https://doi.org/10.3389/fevo.2020.00235>
3. R. Font, A. Gálvez, J. Moltó, A. Fullana and I. Aracil, *Chemosphere*, **78**, 152 (2010); <https://doi.org/10.1016/j.chemosphere.2009.09.064>
4. J. Poerschmann, B. Weiner, S. Wozidlo, R. Koehler and F.D. Kopinke, *Chemosphere*, **119**, 682 (2015); <https://doi.org/10.1016/j.chemosphere.2014.07.058>
5. P. Zhao, T. Li, W. Yan and L. Yuan, *Environ. Technol.*, **39**, 977 (2018); <https://doi.org/10.1080/09593330.2017.1317841>
6. W. Schmidt, In Proceedings of National Poultry Waste Management Symposium, Auburn, USA, pp. 276-282 (1998).
7. M.N. Acda, Sustainable Use of Waste Chicken Feather for Durable and Low Cost Building Materials for Tropical Climates, Nova Science Publisher Inc.: New York, pp. 353 (2016).
8. T. Kornilowicz-Kowalska and J. Bohacz, *Waste Manag.*, **31**, 1689 (2011); <https://doi.org/10.1016/j.wasman.2011.03.024>
9. C. Mullins and M.S. Tite, *J. Geophys. Res.*, **78**, 804 (1973); <https://doi.org/10.1029/JB078i005p00804>
10. A. Lilliestrale, Thesis, Molecular Biotechnology Programme, Uppsala University, Uppsala, Sweden (2007).
11. M. Muslem, A. Kuncaka, T.N. Himah and R. Roto, *Indonesian J. Chem.*, **19**, 835 (2019); <https://doi.org/10.22146/ijc.29801>
12. M.H.B. Hayes and R.S. Swift, The Chemistry of Soil Organic Colloids, eds.: D.J. Greenland and M.H.B. Hayes, The Chemistry of Soil Constituents, Wiley: Chichester, pp. 179 (1978).
13. A. Piccolo, *Adv. Agron.*, **75**, 57 (2002); [https://doi.org/10.1016/S0065-2113\(02\)75003-7](https://doi.org/10.1016/S0065-2113(02)75003-7)
14. American Public Health Association (APHA), Standard Methods for the Examination of Water and Wastewater, New York (1975).
15. E.J. Park, B.C. Park, Y.J. Kim, A. Canlier and T.S. Hwang, *Macromol. Res.*, **26**, 913 (2018); <https://doi.org/10.1007/s13233-018-6123-z>
16. S. Sharma, A. Gupta, S.M. Saufi, C.Y. Gek Kee, P.K. Podder, M. Subramaniam and J. Thuraisingam, *IJUM Eng. J. (N.Y.)*, **18**, 47 (2017); <https://doi.org/10.31436/ijumej.v18i2.806>
17. G. Gasco, J. Paz-Ferreiro, M.L. Álvarez, A. Saa and A. Méndez, *Waste Management*, **79**, 395 (2018); <https://doi.org/10.1016/j.wasman.2018.08.015>
18. Y.N. Vodyanitskii, S.N. Lesovaya and A.V. Sivtsov, *Eurasian Soil Sci.*, **34**, 774 (2001).
19. Y. Qi, J. He, F. Xiu, W. Nie and M. Chen, *J. Clean. Prod.*, **196**, 331 (2018); <https://doi.org/10.1016/j.jclepro.2018.06.074>
20. A.C. Garcia, F.G. Izquierdo and R.L.L. Barbara, Emerging Technologies and Management of Crop Stress Tolerance, Elsevier: Amsterdam, pp. 449 (2014); <https://doi.org/10.1016/B978-0-12-800876-8.00018-7>