

Full Length Research Paper

Effects of extraction period on yield of rice straw compost humic acids

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Accepted 20 January, 2012

Humic acids (HA) are widely used in agriculture because of their capability as chelator, organic matter, soil improver and growth promoter. However, their isolation differs in terms of origin or source because of wetting and solubilization factors. This study was conducted to determine extraction period for HA from composted rice straw. Standard procedures were used to extract HA from rice straw compost at different extraction periods of 4, 8, 12, 16, 20 and 24 h. At the end of each extraction period, samples were centrifuged, followed by fractionation and purification. HA yield at different extraction periods was determined and the HA samples were analyzed using standard procedures. The relationship between extraction period and rice straw compost HA yield was quadratic. Extraction period for rice straw compost was 21.6 h and purification (done within 1 h) using distilled water was effective in removing impurities. Moreover, the HA produced at different extraction periods were similar in terms of chemical and spectral characteristics. HA from rice straw compost can be extracted within 24 h and purification can be done in relatively short time without changing their chemical and spectral properties to produce K-humate.

Key words: Humic acids, rice straw compost, spectral characteristics, extraction period, fractionation period.

INTRODUCTION

Humic acids (HA) are useful organic compound acids in agriculture. A previous study has reported that planting on HA treated soil increased root structure (Zandonadi et al., 2007). Also, maize seedlings treated with HA had increased secondary root proliferation, cell elongation and formation of root fine hairs (Canellas et al., 2002), thereby enhancing root surface area for nutrient uptake and use efficiency. Moreover, plant growth rates are directly affected by humates (salt of HA) application (Atiyeh et al., 2002; Mosley, 2006). Addition of HA showed increase in seed germination (Palazzo et al., 2008; Lazcano et al., 2010; Loffredo et al., 2010). A previous study reported almost 100% increase in yield of tomato plants upon application of humates (Zimmer, 2004).

Humic acids can be isolated from various natural

sources such as tropical peat (Huey et al., 2010; Rosliza et al., 2009; Yusuff et al., 2009; Kasim et al., 2007), ombrotrophic peat bog (Zacccone et al., 2009; Zacccone et al., 2008; Gondar et al., 2006), coal (Zheng et al., 2010; Reeza et al., 2009; Arslan and Pehlivan, 2008; Lorenc-Grabowska and Gryglewicz, 2005), etc. Humic acids are also isolated from various composts produced from pineapple leaves (Ahmed et al., 2004), sago waste (Petrus et al., 2009), sewage sludges, manure and worm compost (Deiana et al., 1990; Canellas et al., 2002), and municipal solid waste compost (García-Gil et al., 2004). The isolation period of HA differs in terms of parent material or source. For instance, extraction of HA from tropical peat (Hemist) is different from that of Saprist (Kasim et al., 2007; Rosliza et al., 2009). A study by Ahmed et al. (2005) found HA extraction period for composted pineapple leaves to be 17 h. HA in some compost have been in extracted 12 h using the method of the International Humic Substance Society (Schnitzer and Skinner, 1982 cited in Canellas et al., 2002).

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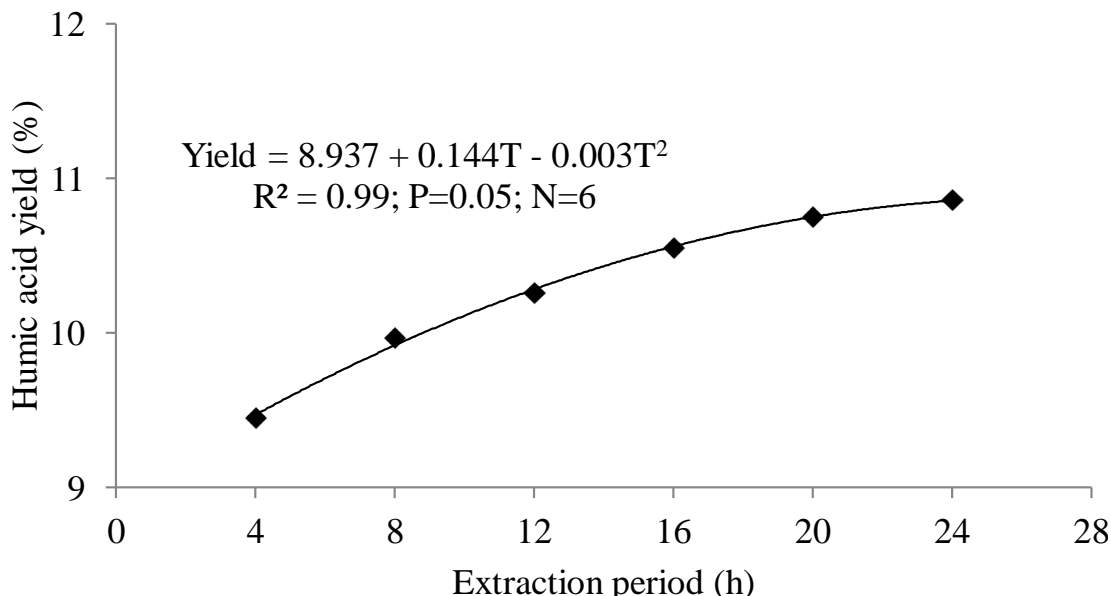


Figure 1. Relationship between extraction period and humic acid yield.

This study was carried out to determine the extraction period for HA in rice straw compost because there is dearth of information on this aspect in Malaysia. It focused mainly on extraction period, since it varies with type of material. Fractionation periods were not determined because previous studies found no significant relationship between fractionation period and HA yield (Ahmed et al., 2005; Kasim et al., 2007; Rosliza et al., 2009).

MATERIALS AND METHODS

The rice straw compost used in this study was from a previous study (Palanivell et al, 2012 under review). The HA extraction was conducted using the procedures described by Ahmed et al. (2004), Stevenson (1994) and Kasim et al. (2007). Ten grams of air-dried compost was placed into a 250 ml polyethylene centrifuge bottle and 100 ml of 0.1 M KOH solution was added. The bottle was stopped with its cap and the mixture was shaken at room temperature (approximately 25°C) using an orbital shaker at 180 rpm with different shaking (extraction) periods. The extraction periods used in this study were 4, 8, 12, 16, 20 and 24 h. At the end of each extraction period, the samples were centrifuged at 10,000 rpm for 15 min. The dark-coloured supernatant liquid was decanted; the pH of the solution was adjusted to 1.0 using 6 M HCl and left at room temperature for 3 h (fractionation). At the end of each fractionation period, the suspension was transferred into polyethylene centrifuge bottle and centrifuged at 10,000 rpm for 10 min. The liquid part (fulvic acid) was kept for further analysis. The HA was purified 5 times as described by Ahmed et al. (2005), using 100 ml distilled water and centrifuged at 10,000 rpm for 10 min to reduce mineral content and HCl during acidification. The supernatant decanted was analyzed for K, Ca, Mg and Na using Atomic Absorption Spectrometer (PerkinElmer AAnalyst 800). After the purification, the HA was oven-dried at 40°C until constant weight was attained, weighed and HA yield expressed as percentage by weight.

HA was characterized for E₄/E₆ using the method of Campitelli and Ceppi (2008) and analyzed using UV-Vis spectrophotometer. Ash and organic carbon contents of the HA were determined using the dry combustion method (Cheftetz et al., 1996). The carboxylic, phenolic functional-group and total acidity of the HA were determined as described by Inbar et al. (1990). Selected cations were extracted by the method described by Cheftetz et al. (1996) and were determined using Atomic Absorption Spectrometer (PerkinElmer AAnalyst 800). Infrared spectra of the HA were recorded on KBr pellets (1 mg of HA plus 100 mg of dry KBr) (Pérez et al., 2008) from 4000 to 600 cm⁻¹ on a Thermo Scientific model Nicolet 380 Fourier Transform Infrared (FTIR) spectrophotometer. Finally, the relationship between extraction period and the yield of HA from rice straw compost was determined using the statistical analysis system (SAS) version 9.2.

RESULTS AND DISCUSSION

The relationship between extraction period and rice straw compost HA yield was quadratic (Figure 1). This observation is consistent with the observation that HA yield increases with increasing extraction period to some extent (Ahmed et al., 2005; Kasim et al., 2007). Besides reduction of high molecular-weight complexes depolymerization, the wetting and solubilization of the rice straw compost increased with increasing extraction period. This could be attributed to the fact that the exchange process between K from the extractant and the exchange sites which consist of hydroxylic, phenolic and carboxylic functional groups of compost progressed with extraction period until a maximum period maximum number of exchange sites might have been saturated with K ions. This extraction process might have made the compost highly soluble. Furthermore, the difficulty of HA extracting at initial shorter period at 4 h, might due to difficulty

Table 1. Chemical properties of humic acid from rice straw compost at different extraction period compared with known values.

Property	Time (h)						Tan (2003)
	4	8	12	16	20	24	
E ₄ /E ₆	8.08	7.72	7.68	7.75	7.68	7.18	7 - 8
Carbon (%)	56.45	56.45	56.84	55.68	56.45	55.29	56 - 62
Phenolic	200.00	183.33	150.00	200.00	233.33	250.00	240 - 540
Carboxylic	350.00	358.33	350.00	350.00	350.00	366.67	150 - 440
Total Acidity	550.00	541.67	500.00	550.00	583.33	616.67	500 - 700
K (%)	0.586	0.359	0.396	0.385	0.391	0.250	nd
Ca (%)	0.075	0.063	0.066	0.060	0.059	0.054	nd
Mg (%)	0.013	0.011	0.016	0.020	0.025	0.020	nd
Na (%)	0.263	0.233	0.257	0.292	0.251	0.223	nd

nd: Not determined.

of wetting the compost, as it have been air-dried. It must be stressed that in a situation where HA characteristics are much more important than the quantity of HA extracted, an optimum extraction period, 21.6 h (less 10% of maximum extraction period of 24 h; resultant to optimum yield of 10.6%) or less could be used, as the longer the extraction period, the greater will be the HA chemical changes (Stevenson, 1994). The optimum extraction period was estimated as 90% of the maximum extraction period (Ahmed et al., 2005; Kasim et al., 2007) equivalent to HA yield of 10.65%, beyond which the yield of HA may not be economical time wise.

Chemical properties of the rice straw compost HA at different extraction period are shown in Table 1. The E₄/E₆, carbon, phenolic, carboxylic content and total acidity values were within the standard range. The different extraction period did not alter the chemical properties of HA drastically. The minimum chemical properties alteration is supported by the infrared spectra in Figure 2, where all the compost HA extracted at different extraction periods were similar. All the HA had bands at 3400 cm⁻¹ (OH and N-H stretch), 2900 cm⁻¹ (aliphatic CH stretch), 1650 cm⁻¹ (C=O stretch of primary amide, aromatic C=C, hydrogen bonded C=O, double bond conjugated with carbonyl and COO⁻ vibrations), 1460 cm⁻¹ (aliphatic C-H, CC-H₃), 1420 cm⁻¹ (COO⁻ anti symmetrical stretch), 1220 cm⁻¹ (C-O stretch, aromatic C-O, C-O ester linkage, phenolic C-OH) and 1120 cm⁻¹ (C-O stretch of polysaccharides) (Tan, 2003; Ahmed et al., 2004). This HA shows similarity with HA extracted from utisols where it has only strong band at 1650 cm⁻¹ and lack of 1720 cm⁻¹ band (Tan, 2003). Hence, HA of rice straw compost extracted at different extraction periods were qualitatively identical.

The impurities were reduced by washing HA using distilled water, and this because the washing reduced the K, Ca, Mg and Na contents (Figures 3, 4, 5 and 6). The K, Ca, Mg and Na contents before HA purification (no washing) were generally high, but they decreased remarkably with first washing and consistently removed from second to fifth washing regardless of different HA extraction period. Apart from removing the cations, the self ionization or dissociation properties of water [2 H₂O (l) ⇌ H₃O⁺ (aq) + OH⁻ (aq)] (Geissler et al., 2001) produces and donate more hydronium and hydrogen ions which could function as Brønsted-Lowry acid, and this might have replaced some of the remaining cations at HA exchange sites that were not replaced by hydrogen ions during acidification using concentrated HCl for HA isolation from fulvic acid. This observation was consistent with a previous study by Ahmed et al. (2004) that distilled water can be used for purification since it is cheaper than chemicals. For confirmation of HA purity, the chemical property and the characteristics of HA were consistent with those spectra reported by Tan (2003), Stevenson (1994), and Inbar et al. (1990).

Conclusion

The relationship between extraction period and HA yield from rice straw compost was quadratic. The maximum and optimum extraction periods of HA from rice straw compost were at 24 and 21.6 h, with 10.67 and 10.65% HA yield, respectively. HA can be purified within 1 h by using distilled water to reduce the ash content and this purification does not change the HA chemical and spectral characteristics. The significance of this study is

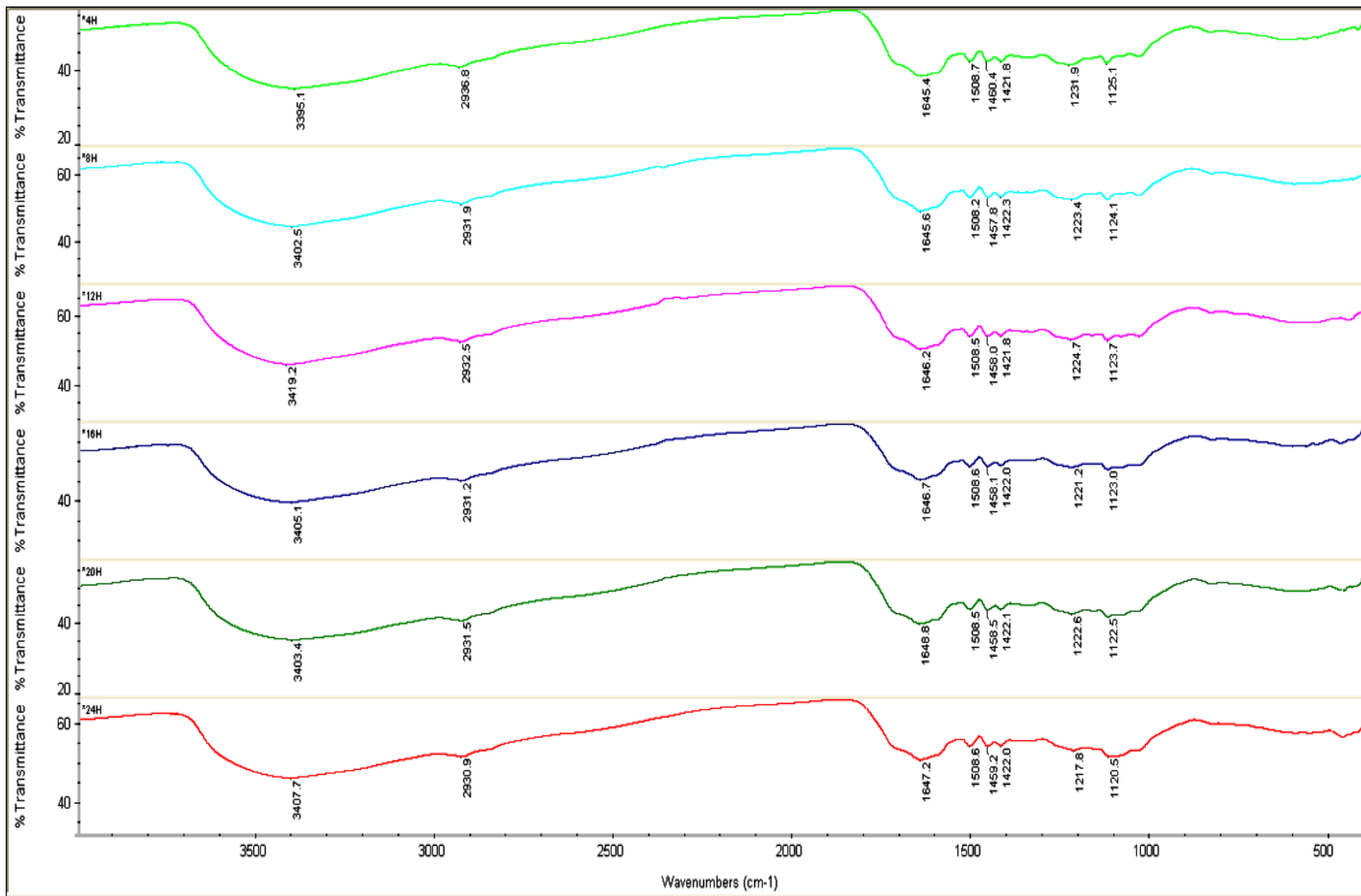


Figure 2. Fourier-transform infrared (FTIR) spectra of HAs with different extraction period.

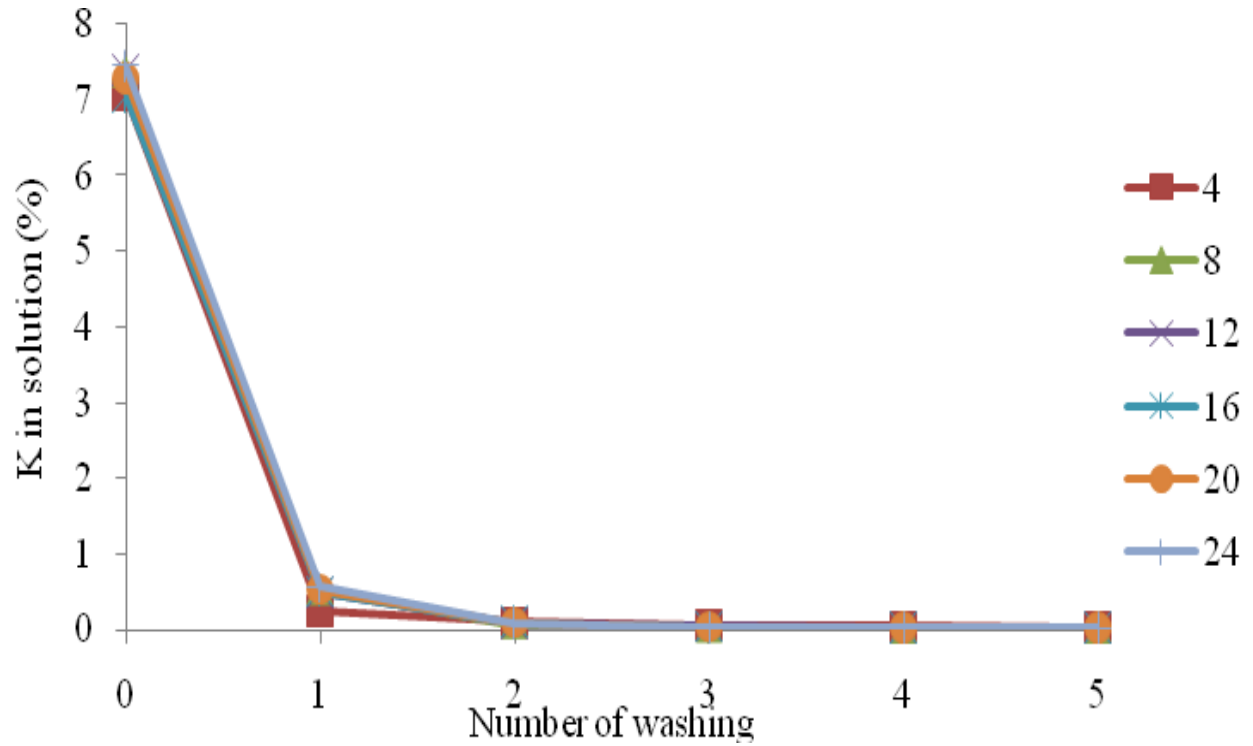


Figure 3. Effect of washing on K removal from rice straw HA.

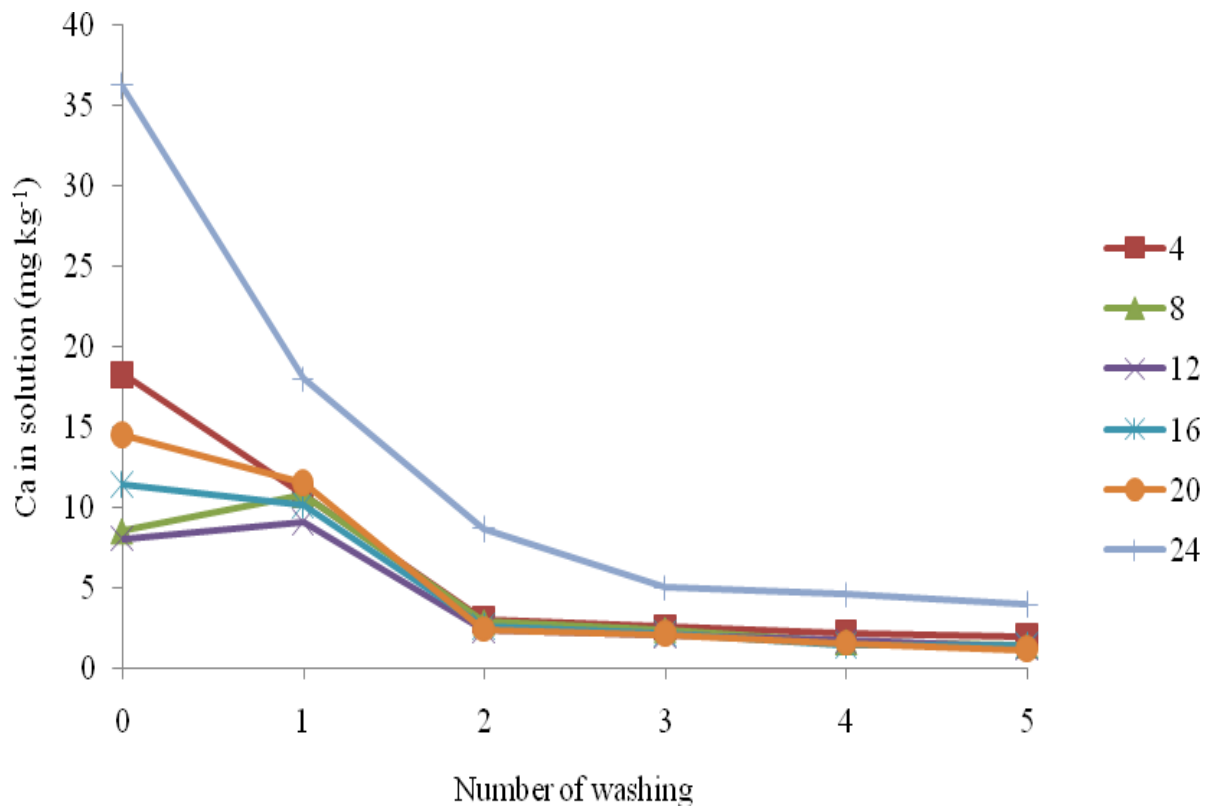


Figure 4. Effect of washing on Ca removal from rice straw HA.

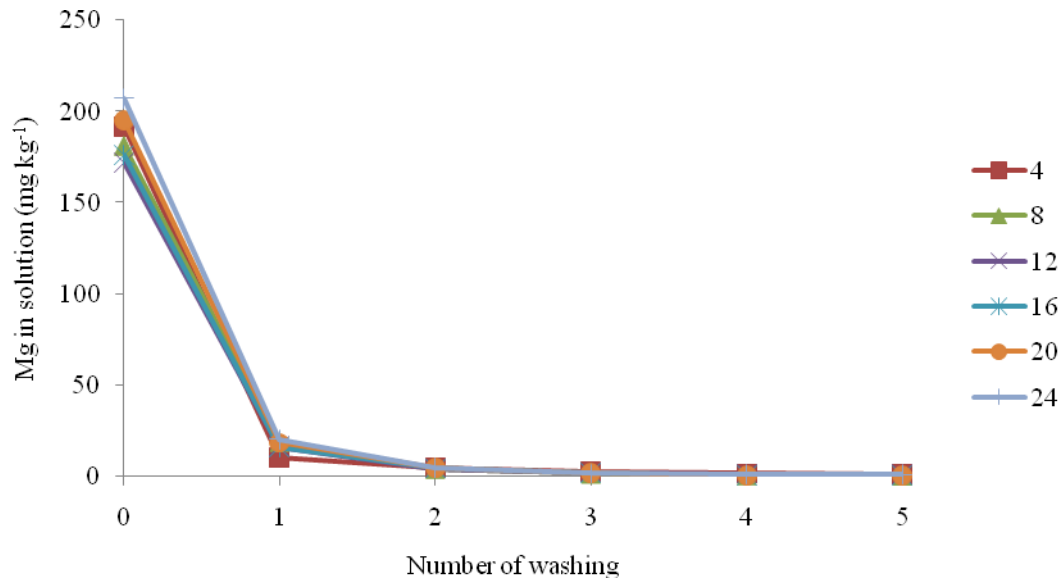


Figure 5. Effect of washing on Mg removal from rice straw HA.

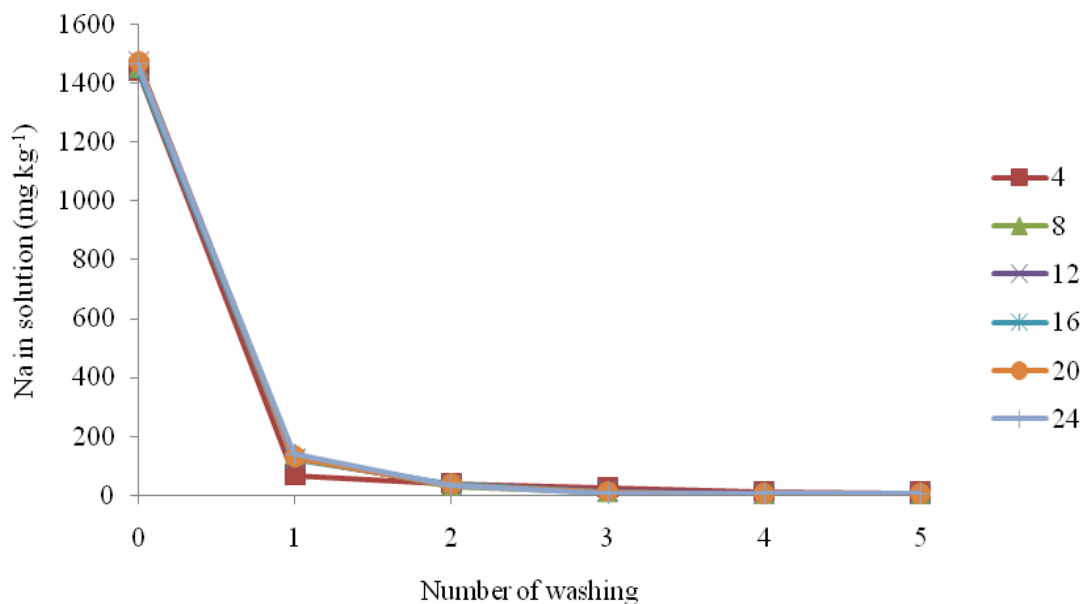


Figure 6. Effect of washing on Na removal from rice straw HA.

that HA from rice straw compost can be extracted within 24 h and purification can be done in relatively short time to produce K-humate.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support of the Ministry of Higher Education Malaysia and Universiti

Putra Malaysia.

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