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Removal of Dissolved Organic Carbon from Peat Swamp Runoff Using Assorted Tropical Agriculture Biomass

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ABSTRACT

In this study, agriculture biomass was used to remove dissolved organic matter from peat swamp runoff. The functional groups and morphological properties of 6 tropical agriculture biomasses (coconut husk, rice husk, empty fruit bunch, sago *hampas*, saw dust and banana trunk) in their raw and citric acid–treated states were examined. The Fourier transform infrared (FTIR) spectra showed that various biomasses were typically characterised with lignocellulosic compounds. The spectra analysis further demonstrated that citric acid treatment resulted in the dissolution of lignin and hemicelluloses to various extents where carboxyl groups were also introduced. These changes hypothetically suggest improved adsorption ability. Treatment of peat swamp runoff with various untreated biomasses showed no adsorption. With the modified biomass, adsorption was evidenced, with rice husk illustrating the highest removal efficiency of 60% to 65%.The biosorbent can be used in the water treatment process especially for treating water with a high dissolved organic matter content. The spent sorbent can be subsequently applied as a soil conditioner as the dissolved organic fraction, commonly known as humic matter, possesses important agricultural value.

Keywords: Agriculture biomass, adsorption, citric acid treatment, dissolved organic matter, peat swamp runoff

INTRODUCTION

In Malaysia, peat soil encompasses 7.45% of the total land area of the country, of which 70% is found in Sarawak, the northern part of Borneo Island (Wetlands International, 2010). The water catchment in this area serves as an important source of freshwater supply to settlements and townships residing in the peatland. According to statistics, an estimated 3,000 million litres of water are extracted annually from the streams tainted by peat swamp leachate throughout Sarawak (McCartney & Acreman, 2009). Typically, the water is yellowish to

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brownish in colour due to the presence of dissolved organic matter and thus, is often called tropical black water. The dissolved organic matter is technically termed as humic substances; it is well known for its agricultural importance as a soil supplement, but its presence could have a significant impact on the treatability of the water. It is often difficult for the conventional water treatment process to remove the organic fraction effectively, which results in the formation of disinfection by-products. In a study by Sim and Mohamed (2005), treated water sourced from peat swamp runoff was found to contain a higher amount of trihalomethanes compared with non-peat water sources. In addition, the tropical humic molecules were found to be more susceptible to electrophilic cleavage, increasing the risk of trihalomethanes (Sim & Mohamed, 2007). Over the years, some treatment plants treating organic-rich water in Sarawak have switched from the conventional sedimentation processes to the dissolved air flotation system. This latter technology is commonly known for its better efficiency, especially in treating humic-rich water; however, it incurs a relatively higher operational cost (van Puffelen *et al*., 1995; Heinänen *et al*., 1995; Edzwald, 2010).

MATERIALS AND METHODS

Sample preparation

The biomasses selected were coconut husk (CH), banana trunk (BT), sago *hampas* (SW), rice husk (RH), oil palm empty fruit bunch (EFB) and saw dust (SD). The biomasses were washed extensively with running tap water and cut into smaller pieces (1-2 cm). They were then oven-dried at 105^{o}C for 24 hrs, and then were ground (< 2 mm) and stored in desiccators. In addition, the biomasses were chemically treated with citric acid in an attempt to improve the adsorption ability. Five grams of biomass were added to 30 mL of 0.8 M citric acid and agitated for 3 hrs under room temperature (25-28^{o}C), then washed and dried. The advantage of citric acid over other alternatives is that it is a weak organic acid that is commonly used in various applications such as food, cosmetics, pharmaceuticals etc. thus, the risk of acute toxicity is low.

Characterisation of agricultural biomass

The functional groups of biomass were analysed using Fourier transform infrared (FTIR). All spectra were obtained on a ThermoScientific FTIR spectrometer (Thermo Nicolet Analytical Instruments, Madison, WI) using the KBr disc method with 2 mg of sample in 100 mg of KBr. The samples were scanned in triplicate with the scanning range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. The morphological characteristics were observed using a scanning electron microscope (Model JEOL JSM-6390LA, Japan) with an accelerating voltage of 5kV at ×500 magnification. The samples were coated with a thin film of conducting materials prior to examination.

Adsorption of dissolved organic carbon

The adsorption of dissolved organic carbon was examined based on the absorbance at 465 nm using a UV-Visible spectrophotometer (Jasco V-360 Spectrophotometer) (Gan *et al*., 2007; Ghabbour& Davies, 2009).Numerous wavelengths have been used for the quantification of natural organic matter, for example, 250, 254, 272, 280, 285, 330, 365, 400, 465, and 665 nm (Hautala *et al*., 2000; Chen *et al*., 2002; Świetlik & Sirkorska, 2005; Zbytniewski & Buszewski, 2005). According to Hautala *et al*. (2000), the absorbance at 465 nm is the most recommended for measurement of the colour in water caused by a given fraction of humic matter. Fundamentally, absorbance corresponds proportionally to the humic content; if adsorption takes place, a reduction in absorbance is anticipated. For the adsorption study, 1g of biomass (treated or untreated) was agitated with 20 mL of humic-rich water collected from the Asa Jaya River with pH 3.5-4 for 15 min. The Asa Jaya River is surrounded by peat swampland where the water is highly coloured. The water was passed through a glass column at a flow rate of approximately 1 mL/min. After treatment, the pH of the water ranged between 2.8 and 3.5 with banana trunk and sago hampas respectively, demonstratingthelowest pH. Note that the operating conditions, including the contact time, flow rate and dosage were optimised for maximal adsorption. The eluate was then collected and the absorbance at 465 nm was recorded in triplicate.

Data analysis

The FTIR spectra were analysed using the peak detection algorithm reported elsewhere, yielding a peak table with rows representing samples and columns indicating the peaks identified (in wave number, cm^{-1}) (Sim & Ting, 2012; Sim *et al*., 2012). Each cell relates to the corresponding peak areas. The resulting peak table of 36 rows and 53 columns was square-rooted and standardised prior to the Principal Component Analysis (PCA) to demonstrate whether the functional group properties of different biomasses are distinguishable (Esbensen, 1998; Brereton, 2009). The t-statistic was employed to identify variables discriminating two groups of samples (Brereton, 2009); typically, variables with higher absolute t-values are concluded to have greater discriminatory abilities. The paired t-test at a confidence level of 95% was used to examine the statistical significance.

RESULTS AND DISCUSSION

Characteristics of treated and untreated biomass

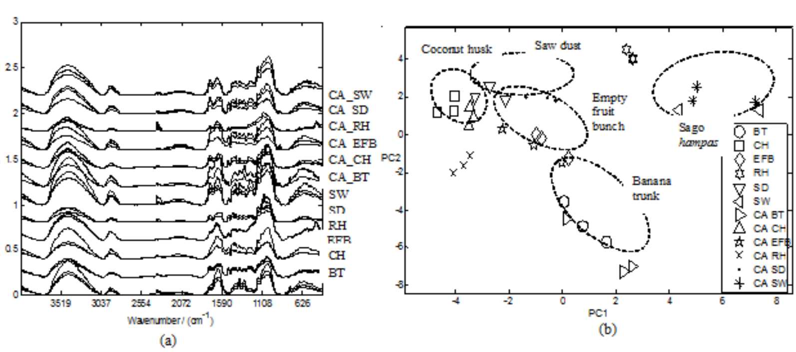


Fig.1: (a) The FTIR spectra of various treated and untreated biomasses; (b) the scores plot of PC2 vs. PC1 prepared with the peak table of FTIR spectra [sago *hampas* (SW); saw dust (SD); rice husk (RH); empty fruit bunch (EFB); coconut husk (CH); banana trunk (BT); citric acid (CA)]

Several absorption bands at 1097 cm^{-1}, 1159 cm^{-1}, 1376 cm^{-1} and 1425 cm^{-1} were observed in various agriculture biomasses. The absorption band at 1159 cm^{-1} was consistently identified; it was assigned to glycosidic linkages that are typical in lignocellulosic compounds (Sim *et al*., 2012). Fig.1(a) shows the FTIR profile of the treated and untreated biomass. The scores plot of the peak table (PC2 versus PC1) in Fig.1(b) demonstrates that different biomasses are distinguishable with citric acid treatment, resulting in some considerable changes, particularly in rice husk. Other biomasses (treated and untreated) remain closely clustered, implying less alteration.

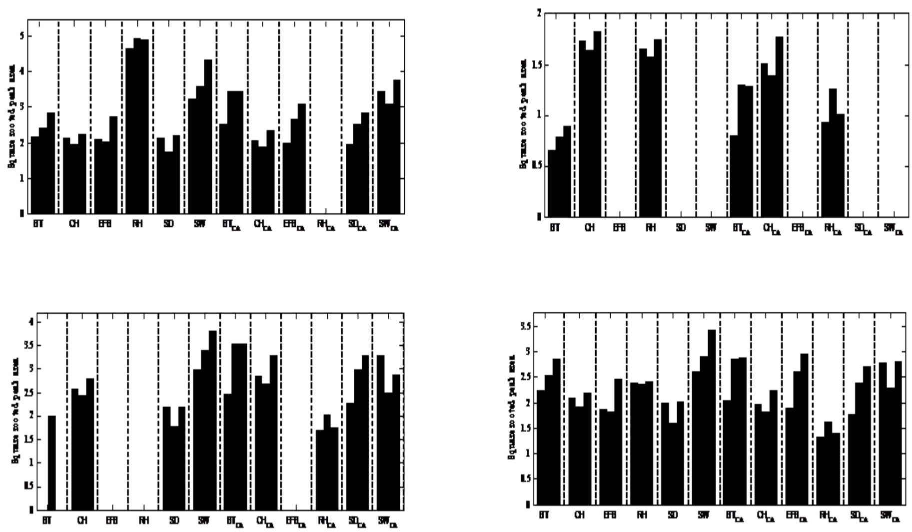


Fig.2: The abundance of important variables distinguishing the untreated and treated biomass

Fig.2 shows the abundance of several important bands discriminating the raw and modified rice husk. The band at 1159 cm^{-1} is completely absent after treatment, indicating extensive hydrolysis. A weak absorption band at 1513 cm^{-1} due to C=C stretching of lignin, on the other hand, is noticeably reduced, implying lignin degradation; this often takes place collectively with hemicelluloses dissolution, which is confirmed by the diminished bands at 1056 cm^{-1}, 1375 cm^{-1} and 1330 cm^{-1} (Peng *et al*., 2009). Ester linkages are anticipated to form upon treatment as a result of the reaction between hydroxyl groups of cellulose and citric acid (Thanh&Nhung, 2009; Farid *et al*., 2010). The reaction is usually corroborated with the presence or increased absorption band at 1750-1730 cm^{-1} ascribed to C=O stretching. This is observable in most treated biomass except empty fruit bunch, suggesting that the material may be less susceptible to treatment. One of the modifications encountered by empty fruit bunch is the shifting of hydroxyl band at 3419 cm^{-1} to 3438 cm^{-1} as a consequence of the breakage of hydrogen bonds in crystalline cellulose, according to Mohkami and Talaeipour (2010). Essentially, the hydrogen bonds can also be found between the polymers forming lignocelluloses i.e. cellulose-hemicelluloses, hemicelluloses-lignin and cellulose-lignin.

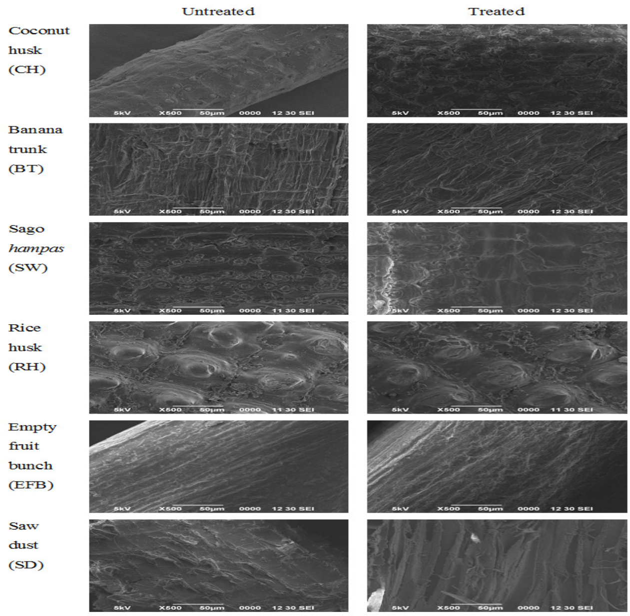
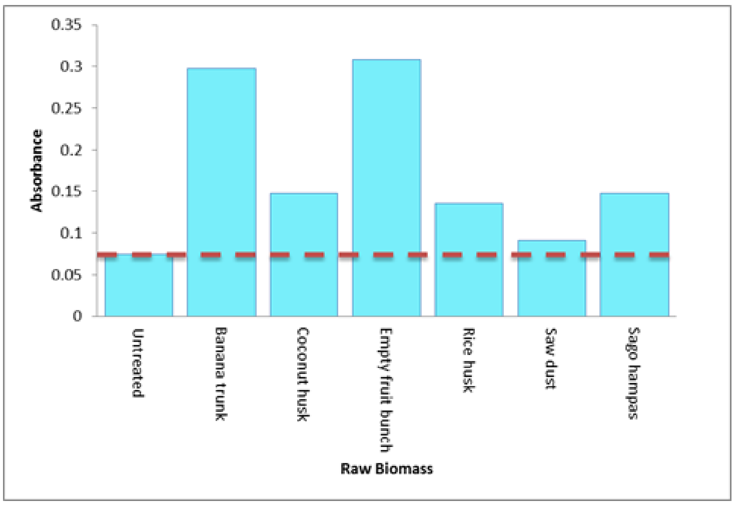


Fig.3: Scanning electron micrographs of various treated and untreated biomasses (×500)

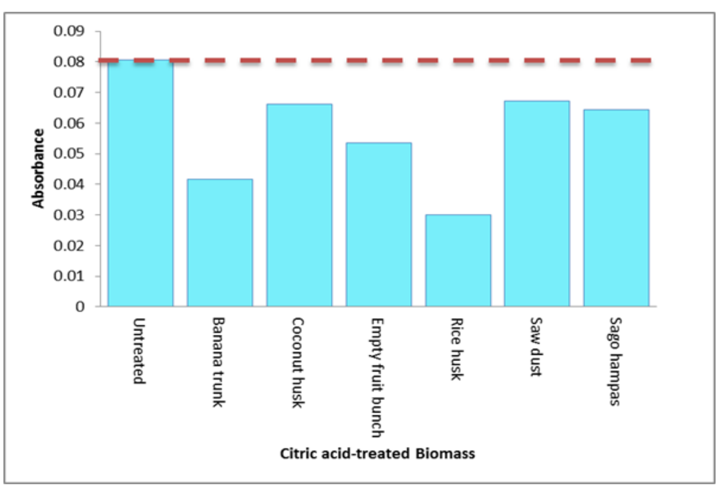
Fig.3 shows the scanning electron micrographs of biomasses before and after treatment. The raw biomass exhibits fibril surfaces; after treatment, some indicate the presence of globular protrusions due to the removal of extractives, waxes and oils (Rout *et al*., 2001; Troedec *et al*., 2008). However, some demonstrate peeled-off surfaces whilst others illustrate minimal disruption. The observations generally suggest that the treatment is rather mild where no extensive damage is seen. Overall, the alterations experienced primarily involve the removal of lignin and hemicelluloses to various extents where carbonyl groups are also introduced; these changes hypothetically suggest improved adsorption abilities.

Adsorption of humic content from the peat swamp runoff

The peat swamp runoff obtained from the Asa Jaya River was subjected to treatment with various untreated and treated biomasses. Fig.4(a) illustrates the absorbance at 465 nm before and after treatment with raw biomass. Apparently, no reduction in absorbance is observed. On the contrary, the treated water demonstrates increased absorbance, suggesting the leaching of lignin, tannins and pigment that have added to the humic content of the water. The results imply that the removal of dissolved organic carbon was unsuccessful, possibly because the active functional sites were concealed within the lignin-hemicellulose matrix. The organic-rich water was alternatively subjected to biomass treated with citric acid; the absorbance of the river water is clearly reduced after treatment (except with the treated banana trunk), suggesting the removal of dissolved organic matter (Fig.4(b)). Among the biomasses, rice husk demonstrates the lowest absorbance, indicating better adsorption performance. The inset of Fig.4(b) shows the appearance of water before and after treatment with rice husk treated with citric acid; the yellowish colour has noticeably decreased. Statistically, it is concluded that the absorbance of rice husk is significantly lower than that of biomasses ($p < 0.05$). Theoretically, the absorbance is proportional to the concentration of dissolved organic carbon; based on this assumption, the removal efficiency of treated rice husk is suggested at approximately 60% to 65%. The superior adsorption ability of modified rice husk is possibly associated with the somewhat extensive changes experienced during treatment.



(a)



(b)

Fig.4: The absorbance of water at 465 nm after treatment with (a) raw biomass and (b) citric acid (CA)-treated biomass (Inset of figure illustrates the water before and after treatment with modified rice husk).

CONCLUSION

Agriculture biomasses in their untreated state are unlikely to be useful as biosorbents for the removal of dissolved organic matter. Additional treatment with citric acid was found to remove the lignin-hemicellulose matrix resulting in the esterification of hydroxyl groups yielding carbonyl functionalised biomass. These changes are experienced by biomasses to various extents. In this study, rice husk appears to be more susceptible to treatment, which in turn results in better adsorption ability with a removal percentage of 60% to 65% based on the absorbance measurements. As a conclusion, the application of agriculture biomass to remove dissolved organic matter could help to improve the existing water treatment process, alleviating the problem due to the naturally occurring trihalomethanes precursors and also reducing the amount of coagulant needed.On the other hand, the spent biosorbent is enriched with humic substances that have been well-established for its beneficial effects in plants, thus, it can be potentially employed as a soil conditioner in agriculture applications.

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