UTILIZATION OF BAMBOO LEAVES WASTES FOR DYES AND SOME HEAVY METALS TREATMENT

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ABSTRACT

The aim of this work was to prepare adsorbent for absorb the toxic substance such as dye and heavy metal by simple preparation method. The 3 methods such as physical , chemical and mixed method were used in the preparation ,then the adsorbent products were tested an adsorption efficiency on dye as Methylene Blue and rhodamineB and heavy metal such as Cadmium and Lead. The results showed that an absorbent from mixed method could be use as an toxic absorbent with the absorption efficiency in the range of 70- 99 %..

Keywords: Bamboo leaves, Waste, Dye, heavy metal

INTRODUCTION

Nowadays, the environment is very importance for our life , all people must aware the side effect from environmental change that impact on people.The agricultural wastes are the one that very important, many research works report to use the waste for treatment of toxic substance. Bamboos are useful plant, all parts of bamboo can used for many purposes such as stem is used as home construction[1] ,furniture[2], bamboo vinegar[3] and bioreinforcement[4]. Baby shoot is also used as delicious food ,leaves used as antioxidant substance source and used as a medicinal material in China to treat inflammation[5],cardiovascular discease[6], crafts, pulp, paper, board, wood-composite products, furniture, and fuel energy. Ming-Xiong He et al,[7] also report that bamboo may be a new source of carbohydrate to produce biorefinery support many works from many researcher[8].

Bamboo belongs to the grass family which is an enduring, versatile and renewable material[9]. Thus the other application of bamboo are presented as charcoal especially activated charcoal to remove toxic substance from natural water[9,10]. The bamboo and bamboo residues can be changed into bamboo charcoal (BC) at high temperature and low oxygen atmosphere. BC has been commercially used in water purification, dehumidification, odor adsorbents and health products. Bamboo is an outstanding renewable biomass resources due to its highly growing speed[11]. Bamboo charcoal was also used to absorb mercury after modification with zinc chloride and heated at 800 ^{o}C for 2 hours under CO2 control atmosphere[12]. Some researcher also prepared as nanotube particle[13] removal heavy metal, but high preparation cost. However, agricultural by-products have received an increasing attention for the production of activated carbons due to their low-cost, renewability and wide prevalence.

Toxic compounds from many industries were interested for many years ago, all those toxic substances can leached to the environment. There have many research works about the toxicity treatment base on adsorbent. In textile industry, the textile dyes were an important source for environmental interference [14]. Heavy metal is the one toxic substance effect on environment too. Many adsorbents have been developed for metal removal such as olive cake, sawdust, pine needles, almond shells, cactus leaves, charcoal used, hazelnut shell,

coconut shell charcoal, banana peel, tamarind peel[15], sugar cane[16],green alga[17],date palm leaflets[18,19] and rice husk[20].

However, bamboo generates large volumes of leaf wastes, which are deposited in landfills or burned in an uncontrolled manner, with negative effects in the environment. In this work, the wastes as bamboo leaves that fallen from their stem were changed to other useful material as an adsorbent material by simple method.The bamboo leaves were modified by physical method , chemical method and mixed method. The modified bamboo structures were checked changing of functional group by Fourier Transform Infrared Spectroscopy and screening surface by Scanning Electron Microscopy.Then, all adsorbent were evaluated their absorption efficiency on dye as methylene blue and rhodamine B dye. Finally, the efficiency absorption of heavy metal such as cadmium and lead were studied too.

MATERIALS AND METHODS

Fallen bamboo leaves (*Bambusa* spp.) were collected from Wangnamkhaew district, Nakornrachasrima Province. Sulfuric acid(AR grade) , nitric acid(AR grade), and acetic acid(AR grade) were purchased from BDH. Sodium hydroxide and Potassium hydroxide were purchased from Merck chemicals. Ammonium hydroxide(AR grade) was purchased from Acros. Distillate Vinegar(commercial grade) was purchased Foodland Supermarket. Methylene blue(AR grade) and rhodamine (AR grade) were purchased from Fluka. Standard cadmium and lead solution (Atomic absorption grade) were purchased from Merck chemicals.

Part 1: Preparation of Bamboo adsorbent samples

The bamboo leaves were cleaned with distilled water and dried at room temperature for one hour.The bamboo leaves were separated into 3 groups for treatments as the following way:

Physical Method

Treatment P 1 ; Bamboo leaves were heated at 700 ^{o}C in electric muffle furnace for 4 hours

Treatment P 2 ; Bamboo leaves were heated at 600 ^{o}C in electric muffle furnace for 6 hours

The ashes were grinded in a agate mortar and pestle and sieved below 45 m.

Chemical Method

Treatment C1 ; Bamboo leaves were digested with 65 % nitric acid for 24 hours and filtered residue leaves out and dried in hot air oven at 120^{o}C for 1 hour.

Treatment C2 ; Bamboo leaves were soaked in 99 % acetic acid and treated as C1

Treatment C3 ; Bamboo leaves were soaked in 98 % sulfuric acid and treated as C1

Treatment C4 ; Bamboo leaves were soaked in 10 % sodium hydroxide and treated as C1

Treatment C5 ; Bamboo leaves were soaked in 10 % potassium hydroxide and treated as C1

Treatment C6 ; Bamboo leaves were soaked in 10 % ammonium hydroxide and treated as C1

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Treatment C7 ; Bamboo leaves were soaked in 5 % vinegar and treated as Treatment C1

Mixed Method

Treatment M1 : Bamboo leaves were soaked in 98 % sulfuric acid for 6 hours and filtered residue leaves out and dried in electric muffle furnace at 500^{o}C for 6 hours.

Treatment M2 : Bamboo leaves were soaked in 98 % sulfuric acid for 48 hours and filtered residue leaves out and treated as M1

Treatment M3 : Bamboo leaves were soaked in 10% potassium hydroxide for 6 hours and filtered residue leaves out and treated as M1

Treatment M4 : Bamboo leaves were soaked in 10% potassium hydroxide for 48 hours and filtered residue leaves out and treated as M1

Part 2: Quality Testing of Bamboo ash characteristic

Physical Test

The ash products from each method were ground and weigh to estimate the yield , then they was chosen a good ashing character as particulate character and color.

Functional Group Test

The ash products were weighed 10 mg and mixed with dried potassium bromide and pour into KBr mold die and press at 15000 psi. The tablet sample was hang on the cell holder of Fourier Transform Infrared Spectrophotometer(FTIR, Perkin Elmer model L1280002)

Surface Analysis

The ash products were prepared as Platinum dope sample to put into the sample holder of Scanning Electron Microscopy (SEM)(Hitachi SU8020)

Part 3: Evaluation on Absorption Efficiency

Dye Absorption Study

The ash products were weighed 0.2xxx g and packed on 2 ml plastic syringe tube.The methylene blue dye 5 ppm was prepared and loaded on the packing syringe. The system was eluted with distilled water and filtrate was collected to measure the absorption efficiency on dye absorption. The filtrate was measured an absorbance by Ultraviolet visible spectrophotometer(Shimadzu UV 2401 PC) and calculated the concentration of methylene blue after passed on packing ash column by using the equation 1)

$$\% \text{ Absorption} = \frac{C_{initial} - C_{final}}{C_{initial}} \times 100 \quad \ldots\ldots\ldots 1)$$

The absorption on rhodamine B was treated in the same way as above and calculated the concentration of rhodamine B after passed on packing ash column by equation 1) too.

Heavy Metal Absorption Study

The ash products were weighed 0.2xxx g and packed on 2 ml plastic syringe tube as in 3.1.The standard cadmium solution 5 ppm was prepared and treated as part3.1 but the absorption of cadmium was measured an absorbance by Atomic absorption spectrometer(AA perkin elmer model AAnalyst300) calculated the concentration of cadmium after passed on packing ash column by equation 1) too. Lead absorption was also studied as above.

Statistical Analysis

In determinations parameters were carried out at least five replicates ,except in adsorbent preparation method the 25 replications were applied and values were averaged. For all statistics, ANOVA and Microsoft Excel were used for calculate and graph presentation in this work.

RESULTS AND DISCUSSION

The ash products from each method showed the difference characteristic in products such as color , texture , surface and also gave difference products yields. An adsorbent ash products ash yields showed in table1.

Table1. Average percentage yields of ash products from each method.

Type of method	*% yields*
P1	9.05 ±1.06
P2	11.21 ± 4.22
C1	6.78 ± 0.58
C2	25.84 ± 1.66
C3	23.09 ± 2.84
C4	77.38 ± 5.49
C5	75.31 ± 5.88
C6	24.87 ± 3.27
C7	25.66 ± 3.25
M1	20.94 ± 1.08
M2	35.88 ± 2.54
M3	75.98 ± 4.13
M4	84.87 ± 5.59

From table1, it showed that the mixed method gave the highest yields of ash products especially in M4. It presented as 84.87± 5.59% since ,the system may effect on some chemical substance that used in digestion bamboo leaves.

However, the physical appearance on each product showed as in table2

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Table2 Physical appearance of ash products

Type of method	*Appearance*	
	Color	*Particle character*
P1	Light grey	Small, dried
P2	grey	Small, dried
C1	black	Coarse, semi-dried
C2	black	Coarse,dried
C3	black	Coarse,dried
C4	black	Coarse,dried
C5	black	Coarse,dried
C6	black	Coarse,dried
C7	black	Coarse,dried
M1	Grey black	Small, dried
M2	Grey black	Small, dried
M3	Grey black	Small, dried
M4	Dark brown	Small, dried

The appearance on ash products have difference color in shade grey to brown, depend on methodology in preparation. Ash products from physical method gave good looking character with look like true ash as light grey. However, the mixed method also gave a reasonable ash products since bamboo leaves pass on chemical substance in digestion step and further with high heating at 500^{o}C gave good ash products as same as using physical method but it save n energy used. The mixed method that used to prepare ash products may be get a silica sol gel as referred by Kien-Woh Kow et al.[24] and showed a characteric like solgel status too.

All ash products were checked a functional group change after modification step by scanning FTIR spectrum and compared with FTIR spectrum of particle of standard silica gel(SiO_2) figure 1.The example of the FTIR spectrum of ash products showed in figure 2 and 3.

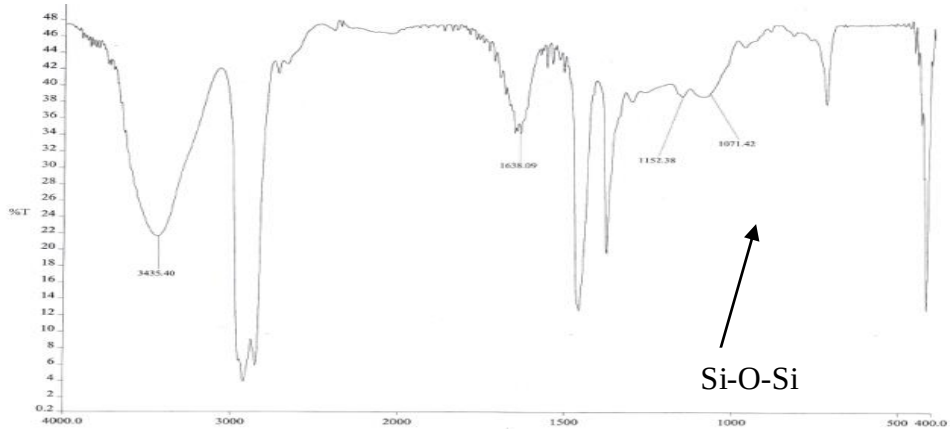

Figure1: FTIR spectrum of standard silica gel

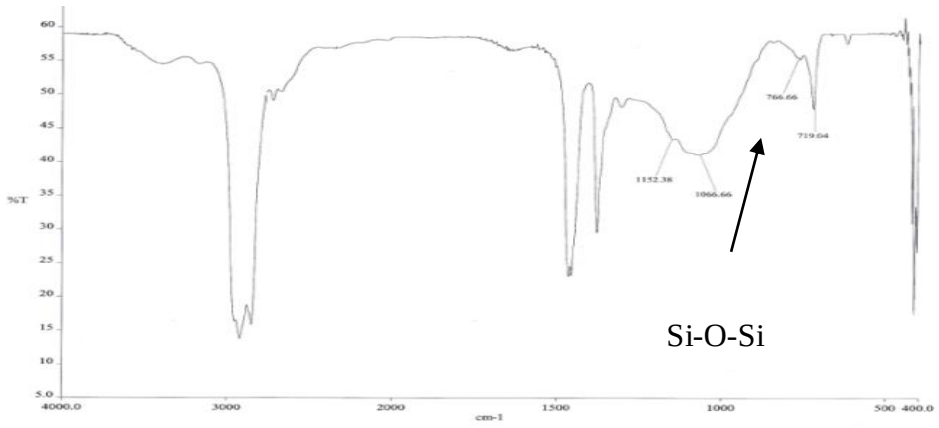

Figure 2. FTIR spectrum of ash product from P1

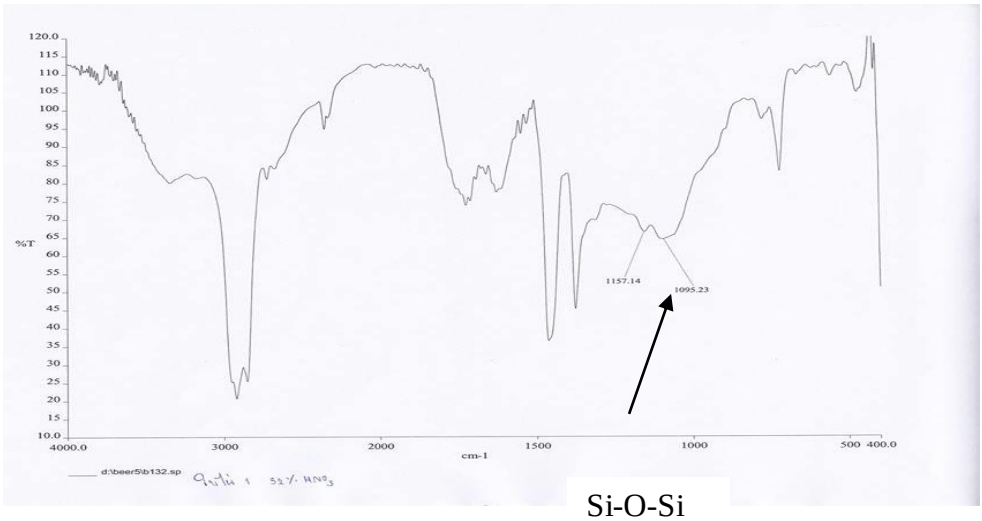

Figure3 FTIR spectrum of ash product from M2

In both figure2 and 3 , showed an important peak at 1100 cm^{-1}which represented Si-O-Si peak. This mean that bamboo leaves could modified its structural and revealed silica peak from common cellulose structure in its leave which support the research result [25] that in bamboo leave contain silica substance in form of silica gel.

However, bamboo ash products from the experiment was selected the best look of ash and scan the SEM to monitor surface compared with normally bamboo leaves as showed in figure 4 -5.

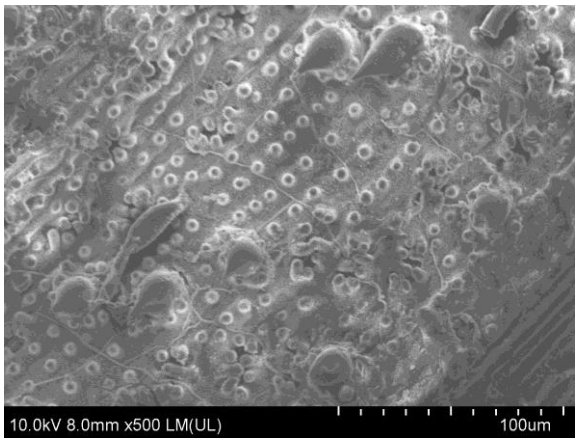

Figure 4 SEM of normally bamboo leaves

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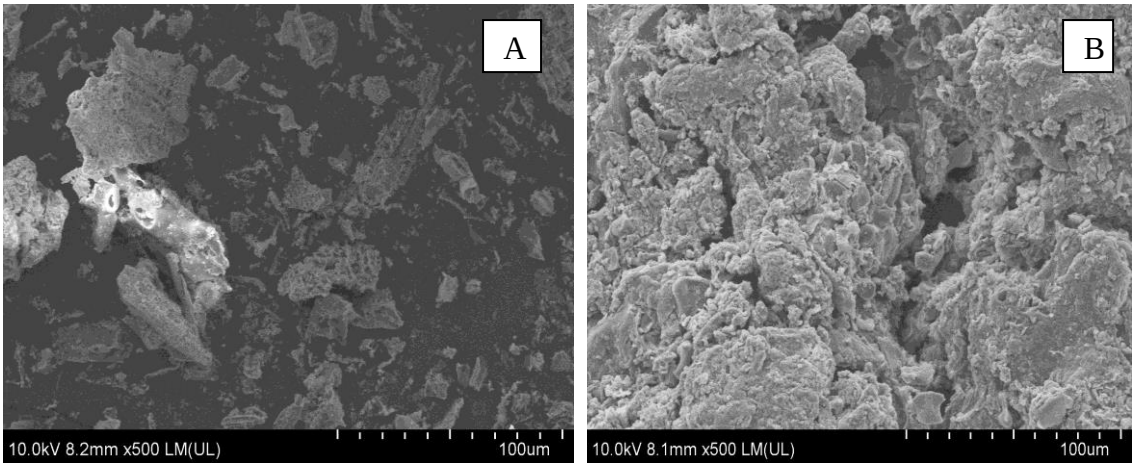

Figure 5. Modified bamboo leave by A) physical method (P1) B) Mixed method (M2)

From above figure 4, the structure of dried bamboo leaves surface in natural showed good structure of fiber but after modification process, it fully changed in their structure especially by physical method. In figure5A , the normal bamboo leaves structure was destroyed and broken into small particle which was known that silica oxide an important component approximately almost 80 % as reffered by Nahar , S. and Hasan , M. [26]and also full of porosity that related with the appearance characteristics in table 2. In figure 5B, it showed the modified structure of bamboo leave still compose of some network in three dimension with also full of porosity too, this seem to give not completely destruction of fiber into small particle since this modified method use a mixed method between sulfuric acid digestion for 48 hrs and followed by burst out acid from its medium after heating at 500^{o}C which were softer condition than using physical method. Its surface also modified and surface oxidized by acid , this step improved the absorption efficiency too[27].

After that those products were selected mixed method products for further study an absorption test on dye and heavy metal. The results showed in table 3 and 4.

Table 3. Absorption efficiency on Dye absorption

Adsorbent type	*absorption efficiency(%)*	
	Methylene blue	*Rhodamine B*
A1	95.35±0.06	96.53±0.17
A2	96.19±0.29	95.39±0.21
A3	99.84±1.612	92.05±2.03
A4	97.68±2.98	90.57±1.62
A5	63.61±0.79	97.51±0.12
A6	64.92±3.45	97.87±0.15
A7	72.37±1.85	97.62±0.13

Note: A1 represent ash product from P1 A2 represent ash product from C3
A3 represent ash product from M1 A4 represent ash product from M2
A5 represent ash product from C5 A6 represent ash product from M3

above abbreviations used in Table 3 and 4

In this part of study,the efficiency of absorption on methylene blue dye and rhodamine B dye of each absorbent showed the absorption efficiency in the range of 63.61 – 99.84% and 90.57- 98.39%,respectively. This results proved that an adsorbent from bamboo leave which were modified in difference method could absorbed dye depend on type of absorbent and type of dye.By the way, A3 was the adsorbent from M1 (Bamboo leaves were soaked in 98 % sulfuric acid for 6 hours and filtered residue leaves out and dried in electric muffle furnace at 500^{o}C for 6 hours) gave highest absorption efficiency in methylene absorption also support the data from Hameed, B.H., et al,[28].The reason for this evidence concerned the time of dipping in acid and heating condition were the optimized condition for absorption condition as referred by Dabroski.A[29]. However, it was noticed that an adsorbent A5-A7 gave the higher absorption efficiency on rhodamine approximately as 97% than others, this may from the effect of alkaline modification method of A5 (ash from bamboo leaves were soaked in 10 % potassium hydroxide and treated as Treatment C1) ,A6 (ash from bamboo leaves were soaked in 10% potassium hydroxide for 6 hours and filtered residue leaves out and dried in electric muffle furnace at 500^{o}C for 6 hours) and A7 (an ash from bamboo leaves were soaked in 10% potassium hydroxide for 48 hours and filtered residue leaves out and dried in electric muffle furnace at 500^{o}C for 6 hours) , potassium hydroxide base destroy cellulose may also be impurity in ash and enhance the absorption of rhodamine dye which was basic dye to tightly form in the ash porosity than using absorption on methylene blue.

Table 4. Absorption efficiency on metal absorption

Adsorbent type	*absorption efficiency(%)*	
	cadmium	*lead*
A1	98.71±1.44	86.67±1.02
A2	99.68±0.46	85.77±1.66
A3	98.87±0.91	86.99±0.58
A4	99.36±0.18	89.99±1.00
A5	98.65±0.46	83.35±0.96
A6	99.77±0.50	88.99±0.98
A7	99.85±0.46	90.55±1.06

Finally, the metal absorption study in cadmium by ash products adsorbent showed more absorption efficiency than lead absorption.This may from the reasons that concern with nature of metal. However,this experiment showed the metal absorption efficiency in the range of 83.35 – 99.85 % , so an adsorbent from bamboo leaves could used as metal absorption from source support the result from [30].

CONCLUSIONS

This work showed the value added of bamboo leaves waste to be an adsorbent on dye and metal. An ash adsorbent was prepared from waste by simple method such as physical method that heating electric muffle at high temperature as other researcher declared(Jian-Zhong Guo[31] ,et al.,2014) , but this method used strong and heat severe condition and required high energy.In this work, the chemical method as declared by Wu et al.[22],(2011) also used to made adsorbent but pure chemical digestion also showed disadvantage point since its passed strong

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acid condition and cellulose fiber of bamboo leaves could not be completely destroy.Thus, the authors also selected the mixed method to modified bamboo leaves structure by treatment with acid as sulfuric acid and alkaline hydrolysis as potassium hydroxide for 6 hrs and 48 hrs in treatment and followed up with heating at 500^{o}C which softer condition than 700 ^{o}C. This mixed method also gave a good products yield and may practical for future use.

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