



# Journal of Applied Sciences

ISSN 1812-5654

**science**  
alert

**ANSI***net*  
an open access publisher  
<http://ansinet.com>

## Study on Biosorption of Heavy Metals by Modified Lignocellulosic Waste

A. Mesfin Yeneneh, S. Maitra and Usama Eldemerdash  
Department of Chemical Engineering, Universiti Teknologi PETRONAS,  
Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

**Abstract:** Heavy metal laden effluent coming out of various industries is posing a huge pressure on the environment. This in turn, necessitates the development of a noble low cost and efficient technology for the removal of such wastes from industrial effluents. In this particular research, the heavy metal (lead (II) biosorption capacity of modified agri-waste (rice husk and sugarcane bagasse) has been studied, taking the two biosorbents as abundant and low cost biosorbents with promising potential to remove hazardous heavy metal wastes from effluent streams. In the study, options to enhance metal sorption capacity by chemical and thermal modification of the sorbents have been investigated. Impact of modifier chemicals used include sodium hydroxide, sulfuric acid, nitric acid, citric acid, acrylic acid and glutamic acid in case of rice husk and modifiers like Sodium Dodecyl Sulfate (SDS), Sodium bicarbonate, Cetyl trimethyl diammonium bromide (CTAB), sodium methylate and urea, in case of sugar cane bagasse in addition to those used with rice husk. Characterization of the sorbents surfaces has been made before and after chemical and thermal modification and after sorption of heavy metals using Fourier Transform Infra-Red Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). Some studies have also been done on mechanism of sorption. In addition impact of concentration of sodium hydroxide and citric acid as effective chemical modifier has been studied. Tests to understand impact of particle size have also been conducted and results for the two biosorbents have been compared.

**Key words:** Biosorption, chemical and thermal modification, agri-waste

### INTRODUCTION

Toxic heavy metals are discharged into the environment from a number of industries such as petroleum, petrochemical, mining, plating, dyeing and metal processing. The presence of heavy metals in the environment has brought about a number of environmental problems. The concentration of heavy metals in wastewater must be controlled so as to meet the water quality standards. Moreover, metal as a kind of resource is getting scarcer. The toxic characteristics of heavy metals can be viewed from different perspectives. First, the toxicity persists for a long time in nature; second, some heavy metals even could be transformed from some how low toxic compounds into more toxic forms under certain environment like mercury; thirdly, the bioaccumulation and bioaugmentation of heavy metal in the food chain could hamper normal physiological activity and ultimately endanger human life; fourthly, technically metals can only undergo change in valence and type of species but cannot be degraded by any methods including biotreatment; lastly, heavy metals could be toxic even with very reduced concentration of about 1.0-10 mg L<sup>-1</sup>. Strong toxic metal ions, like as Hg and Cd,

are extremely toxic even in lower concentration ranges of 0.001-0.1 mg L<sup>-1</sup> (Volesky, 1990; Wang, 2002). Because of the extensive application and the aforementioned immutable character, heavy metal pollution has become one of the most pressing environmental problems presently. Conventional technologies for removal of metal ions from aqueous solution have been studied in detail, such as chemical precipitation, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon, clay etc. Nevertheless, chemical precipitation and electro chemical treatment are ineffective, particularly for lower metal ion concentration in aqueous solution in the range of 1 to 100 mg L<sup>-1</sup>; large amount of sludge to be treated is another demerit of these treatment techniques. Ion exchange, membrane technologies and activated carbon adsorption process are tremendously expensive, especially when dealing with huge volumes of water and wastewater containing heavy metal in low concentration, so they cannot be used at large scale. A potential alternative metal removing process is biosorption which utilizes various natural materials of biological origin, including microorganisms (bacteria, fungi, yeast, algae, etc.) and a variety of natural sorbents of plant origin. These biosorbents have metal

sequestering properties and would help to reduce the concentration of heavy metal ions in solution from ppt to ppb level. They can effectively, efficiently and rapidly sequester dissolved metal ions out of dilute complex solutions. Hence, biosorption is a noble candidate for the removal of heavy metals from huge volume and low concentration complex wastewaters (Veglio and Beolchini, 1997). Heavy metal removal by biosorption has been extensively investigated during the last several decades. Some review papers have already been concentrating on different aspects of heavy metal biosorption (Davis *et al.*, 2003; Kapoor and Viraraghavan, 1995; Kratochvil and Volesky, 1998; Malik, 2004; Tsezos, 2001; Veglio and Beolchini, 1997; Volesky and Holan, 1995). From such reviews, we can deduce that the research on biosorption is dealing with the following three major fields.

First, concerning the biosorbents, it is important to continue to search for and select the most effective and workable types of biomass from an extremely large pool of readily available and inexpensive biomaterials (Kratochvil and Volesky, 1998). Second, the mechanism of biosorption involved in the metal biosorption is only understood to a very limited degree currently. It is necessary to propose a viable mechanism for the metal uptake by biosorbents and understand sorbent-metal interactions. Third, the biosorption research is actually at lab scale. It has been a great challenge to apply the biosorption process into large scale industrial practice (Tsezos, 2001). So far several potential biosorbents with high metal-binding capacity have been identified in part. The application of such waste derived, low cost biological material as biosorbents for the removal of heavy metals is to kill two birds with one stone. For it uses waste to dispose waste. The enterprises can sell their waste biomass and earn some money, at the same time, they can save the cost associated with disposing the waste biomass they produced. There are certain inherent demerits of using microorganisms for the biosorption of heavy metals/dyes. First and for most, the protein rich algal and fungal biomass projected as metal/dye biosorbents have limitations as proteinaceous materials are likely to putrefy under moist conditions. Furthermore, most metal/dye sorption reported in literature is based on algal and fungal biomass which must be cultured, collected from their natural habitats and pre-processed, if available as discards and transported under special conditions, thus introducing the factor of additional costs (Kumar and Bandyopadhyay, 2006). Recently, attention has been diverted towards the biomaterials which come out as byproducts or wastes from large scale industrial operations and agricultural waste materials. The major

advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement and regeneration of biosorbents and possibility of metal recovery. Agricultural materials mainly those containing cellulose and lignin show potential metal binding capacity. The basic components of the agricultural waste biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, starch containing variety of functional groups that facilitates metal complexation or precipitation and which assists the heavy metals sequestration process (Bailey *et al.*, 1999). Ecofriendly and economical agricultural waste materials that are of unique chemical composition, abundance, renewable nature, low in cost and more efficient seem to be viable option for heavy metal remediation. Studies reveal that various agricultural waste materials such as rice bran, rice husk, wheat bran, wheat husk, saw dust of various plants, bark of the trees, groundnut shells, coconut shells, black gram husk, hazelnut shells, walnut shells, cotton seed hulls, waste tea leaves, Cassia fistula leaves, maize corn cob, jatropa deoiled cakes, sugarcane bagasse, apple, banana, orange peels, soybean hulls, grapes stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans, arjun nuts and cotton stalks etc. has been tried and were found to have significant metal sorption capacity. These promising agricultural waste materials can be used in the removal of metal ions either in their natural form or after they undergo some physical or chemical modification (Sud *et al.*, 2008).

Rice husk can be used to treat heavy metals in the form of either untreated or chemically and thermally modified forms using different modification methods. Hydrochloric acid, sodium hydroxide, sodium carbonate, epichlorohydrin (Kumar and Bandyopadhyay, 2006) and tartaric acid (Wong *et al.*, 2003a, b) are commonly used in the chemical treatment of rice husk. Pretreatment of rice husks can remove lignin or entrains separation of structural linkage or decrease degree of polymerization, reduce or remove hemicelluloses or reduce cellulose cristalinity. The heavy metal ions studied so far include Cd, Pb, Zn, Cu, Co, Ni and Au. Different workers have tried the workability of different bases, acids and surfactants as chemical modifiers and thermal activation to enhance the sorption capacity of sugar cane bagasse and rice husk. Citric acid, Sodium Hydroxide, Sodium bicarbonate, Epichlorohydrin, Sulfuric acid, Nitric acid, Tartaric acid, Phosphoric acid Formaldehyde, Potassium Carbonate, SDS have been used as modifiers and resulted in increased sorption of heavy metals (Garg *et al.*, 2009; Ngah and Hanafiah, 2008; Kumar and Bandyopadhyay, 2006; Wong *et al.*, 2003b).

Kumar and Bandyopadhyay (2006) tried three different modification methods for cadmium uptake by water-washed, HCl treated and NaOH treated rice husk. Then based on the output of these tests, they investigated two more chemical modifications i.e., Epichlorohydrin and sodium bicarbonate treated rice husk. The chemical modification resulted in increasing the Cd (II) uptake of raw rice husk 97, 80 and 97% for sodium hydroxide modified rice husk, epichlorohydrin modified rice husk and sodium bicarbonate modified rice husk, respectively. Abdel-Ghani and Elchaghaby (2007) found out that removal of the poisonous lead ions from solutions was possible using rice husk, maize cobs and sawdust as adsorbents, rice husk being the most effective. The removal reached 98.15% of Pb at room temperature. Pyrolysis of rice husk followed by  $H_3PO_4$  impregnation and activation at high temperatures (700-900°C) produced activated carbon with a surface area of  $450\text{ m}^2\text{ g}^{-1}$ . Activated carbon produced by chemical activation with KOH or  $H_3PO_4$  achieved high yield and removal efficiencies comparable to those of commercial products. Sugarcane bagasse consists of cellulose (50%), polyoses (27%) and lignin (23%). The presence of these three biological polymers causes sugarcane bagasse rich in hydroxyl and phenolic groups and these groups can be modified chemically to produce adsorbent materials with new properties. Karnitz *et al.* (2007) reported the use of succinic anhydride modified sugarcane bagasse for treatment of Cu, Cd and Pb from aqueous solutions. The study on chemically modified plant wastes for heavy metal removal has attracted the attention of more scientists. A wide range of low-cost adsorbents obtained from chemically modified plant wastes has been studied and most studies were focused on the removal of heavy metal ions such as Cd, Cu, Pb, Zn, Ni and Cr (VI) ions. The most common chemicals used for treatment of plant wastes are acids and bases. Chemically modified plant wastes vary greatly in their ability to adsorb heavy metal ions from solution. Chemical modification in general improved the adsorption capacity of adsorbents probably due to higher number of active binding sites after modification, better ion-exchange properties and formation of new functional groups that favour metal uptake. Since modification of adsorbent surface might change the properties of adsorbent, it is recommended that for any work on chemically modified plant wastes, characterization studies involving surface area pore size and porosity should be carried out. In this respect, this research work is geared towards investigating the sorption capacity of chemically and thermally modified agro-wastes (rice husk and sugarcane bagasse), impact of

concentration of chemical modifier and particle on sorption capacity and attempts to provide some explanation about the mechanism of sorption and the relationship between surface characteristic and lead sorption capacity of rice husk and sugar cane bagasse in a comparative manner.

## MATERIALS AND METHODS

Materials used as sorbent are agricultural waste materials (rice husk, sugarcane bagasse) that were obtained from local market. Analytical grade chemicals sodium hydroxide and nitric acid have been used for pH adjustment and chemical modification of the sorbent. Lead (II) nitrate has been used for standard metal solution preparation. Inorganic acids like nitric acid and sulfuric acid and organic acids like acrylic acid, citric acid and glutamic acid, has been used for chemical modification conjointly with surfactants like, Sodium Do-decyl Sulfate (SDS) poly acryl amide (PAA), CTAB and other chemicals like urea and sodium methylate, to enhance sorption capacity.

**Preparation of the raw materials:** Raw materials obtained from the local market have been washed thoroughly by tap water and later by deionized water and dried in an oven.

**Study on impact of chemical modifiers:** A variety of inorganic and organic modifying chemicals have been used to important chemical functional groups like, hydroxyl, carboxylic acid, carbonyl and phosphate and amine groups. The raw materials prepared as shown in section above, have been treated with different concentrations of the chemical agents at different temperatures in order to activate the surface functional groups, decrease cristalinity of cellulose and reduce Legnin. Sodium hydroxide at different concentrations of 0.5, 0.6, 0.8 and 1M has been used to treat rice husk for a period of 24 h after which the rice husk samples were rinsed and dried for further treatment with sulfuric acid (1M, 80°C), nitric acid (1M, 60°C), citric acid (0.5%w/w, 1%w/w, 45°C), acrylic acid (1M, 45°C) and Glutamic acid (0.1M) then the samples were rinsed until neutral pH is assumed and the samples have been dried and stocked for further heavy metal removal tests and analysis. Like wise, Sugarcane Bagasse washed and dried has been treated by citric acid (0.5%w/w, 0.1%w/w), sodium hydroxide (0.5 M), nitric acid (1M), sulfuric acid (1M), Sodium Methylate (1% v/v), SDS (1%v/v), CTAB(1%w/w), Urea (1%w/w), PAA (1%w/w) Glutamic acid (0.1M), Sodium Bicarbonate

(0.1 M) for 24 h at 80°C then rinsed with distilled water, dried and used for further heavy metal removal tests and analysis.

**Study on impact of thermal modification:** Two gram treated samples of sugar cane bagasse and rice husk were put into the furnace preheated to 700°C burned into ash for 1 h then stocked for characterization study on SEM, FTIR and heavy metal removal tests.

**Study on particle size:** Ground and treated samples of both rice husk and sugarcane bagasse have been mounted on a sieve tower and have been classified into fraction of size classes ranging from (500-1000 µm) to (45-63 µm). All other parameters were kept constant (pH, 5-5.3, Agitation Speed, 175 rpm, Temperature, 25°C). Then each class has been tested for heavy metal removal capacity.

**Study on mechanism of sorption:** In order to properly understand mechanism of sorption Fourier Transform Infrared Spectrophotometry (FTIR) analysis and Scanning Electro Microscope (SEM) investigation have been done before and after sorption of the lead for the most effective chemical modifiers and thermal modification. All heavy metal removal tests were done by taking 100 mL of 100 mg L<sup>-1</sup> of Pb (NO<sub>3</sub>)<sub>2</sub> solution contacted with the specific sorbent under consideration and with agitation speed of 175 rpm, pH of 5-5.3 and varying contact time according to the type of test under consideration.

## RESULTS AND DISCUSSION

**Impact of chemical modification:** Test on the modification capacity of various chemicals like impact of sodium hydroxide as modifier at different concentrations and later by nitric, sulfuric and acrylic acids has been conducted on rice husk in addition the heavy metal sorption capacity of citric acid and glutamic acid modified rice husk has also been investigated. On the other hand, impact of urea, Sodium Dodecyl Sulfate (SDS), Cethyl-Tri Methyl diammonium bromide (CTAB), sodium methylate, nitric acid, sodium hydroxide, sodium bicarbonate, citric acid and glutamic acid as modifiers of sugarcane bagasse for the removal of lead has also been studied. The lead sorption capacity of raw rice husk, sodium hydroxide (0.5, 0.6, 0.8M) modified, sodium hydroxide and later sulfuric acid, nitric acid, acrylic acid modified and citric acid and glutamic acid modified rice husk was found to be 53, 78.9, 75.8, 72.8, 106.3, 59.4, 51.3, 57.9 and 54 mg g<sup>-1</sup>, respectively. Where as the lead sorption capacity of raw sugar cane, sulfuric acid, SDS, citric acid (0.5 and 1 M),

sodium hydroxide, urea, CTAB, sodium bicarbonate, poly acryl amide, sodium methylate and glutamic acid modified sugar cane bagasse was found to be 89.8, 142.7, 56.4, 108.9, 125.6, 69.3, 52.4, 55.6, 65.8, 54.3, 118.23 and 52.9 mg g<sup>-1</sup>, respectively.

The lead sorption capacity of rice husk has been significantly improved by sulfuric acid and sodium hydroxide. Besides, moderate improvement has also been achieved by nitric acid, citric acid and glutamic acid (Fig. 1). The significant improvement in lead sorption capacity of rice husk may be attributed to the reduction in the complex structure of legnin or removal of low molecular legnin compounds and decrease in cristalinity of cellulose which exposes important functional groups for lead removal. On the other hand, significant improvement in sorption capacity of sugarcane bagasse has also been achieved by sulfuric acid, sodium methylate and citric acid.

However, other chemicals like SDS, CTAB, urea, poly acryl amide resulted in reduction of lead removal capacity of the raw sugarcane bagasse (the raw showed better sorption) (Fig. 2) may be due to the alteration of the ion exchange environment. In general, the sorption capacity of sulfuric acid modified rice husk citric acid, sodium methylate and sulfuric acid modified sugarcane bagasse is much greater than sorption capacity of rice husk and sugar cane bagasse reported in other literature. This may

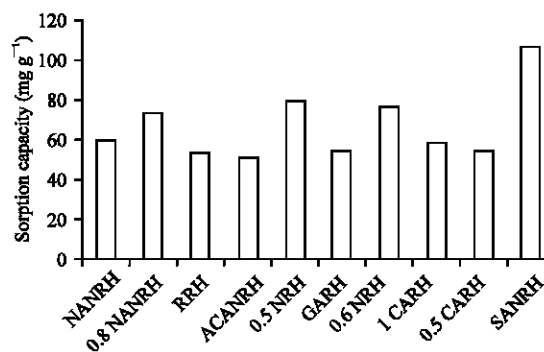


Fig. 1: Impact of Different Modifiers on Lead Sorption Capacity of Rice Husk. NANRH (Nitric acid and Sodium hydroxide modified rice husk), 0.8NRH (0.8M sodium hydroxide modified rice husk) RRH (Raw Rice Husk), ACANRH (Acrylic acid and Sodium Hydroxide modified rice husk), 0.5NRH (0.5M Sodium Hydroxide modified rice husk) GARH (Glutamic acid modified rice husk) 0.6NRH (0.6 M Sodium Hydroxide modified rice husk), 1CARH (1M citric acid modified rice husk), 0.5CARH (0.5M Citric acid modified rice husk), SARH (Sulfuric acid modified rice husk)

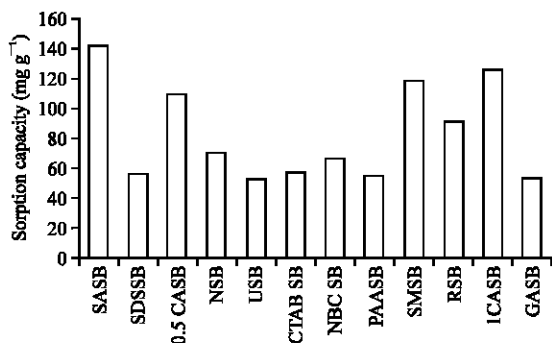


Fig. 2: Lead sorption capacity of sugarcane bagasse after modification by different chemicals. SASB (sulfuric acid modified sugarcane bagasse), SDSSB (sodium dodecyl sulfate modified), 0.5 CASB (0.5M citric acid modified), NSB (sodium hydroxide modified), USB (urea modified), CTAB (Cetyl tri methyl diammonium bromide modified), NBCSB (sodium bicarbonate modified), PAASB (poly acryl amide modified), SMSB (sodium methylate modified), RSB (raw sugarcane bagasse), ICASB (1M citric acid modified sugarcane bagasse), GASB (glutamic acid modified)

be due to formation of new functional groups and increase in the number of binding sites and better ion exchange achieved after modification.

**Impact of concentration of chemical modifier:** The increase in concentration of sodium hydroxide from 0.5 to 0.8 M has resulted in decrease of sorption capacity of rice husk from 78.9 to 72.8 mg g<sup>-1</sup> (Fig. 3). Where as, increase in concentration of citric acid as chemical modifier from 0.5 to 1 M has resulted in increase of lead sorption capacity of rice husk from 54.1 to 57.9 mg g<sup>-1</sup> and sugar cane bagasse from 108.9 to 125.6 mg g<sup>-1</sup>. The increase in concentration of sodium hydroxide has resulted in decrease of sorption capacity because of the chemical alteration or destruction of important functional groups in cellulose or lignin or other materials in the rice husk. Where us, the increase in sorption capacity with increase in concentration of citric acid is related to increase of the essential functional group for sorption, carboxylic acid which is believed to be imparted by citric acid.

**Impact of thermal modification:** The thermal modification of both rice husk and sugarcane bagasse has significantly increased the surface area and important functional groups like hydroxyl from Si-OH and Si-O-Si have been exposed due to the burning of the raw samples into ashes

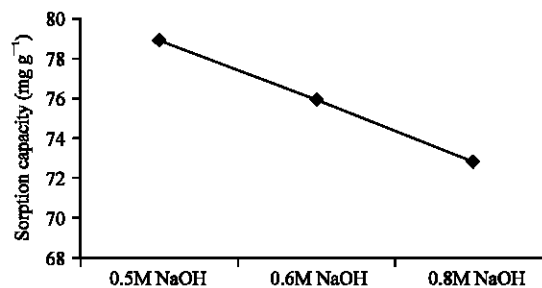


Fig. 3: Impact of concentration of NaOH on sorption capacity of Rice husk

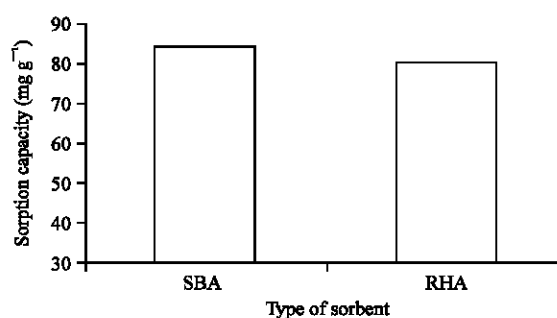


Fig. 4: Lead sorption capacity of Sugarcane Bagasse Ash (SBA) and Rice Husk Ash (RHA) burned at 700°C

which dominantly contains such functional groups. The image from the Scanning Electro Microscope (SEM), Fig. 5a and b and Fig. 6a and b clearly show the improvement in surface morphology and roughness. The lead sorption capacity of sugarcane bagasse ash (84.1%) was found to be better than that of rice husk ash (80.5%) (Fig. 4).

**Impact of particle size:** Particle size of sorbent is also another important factor to be considered in biosorption research. The sorption capacity of rice husk particles in the size range of (45-63 μm) gave better sorption capacity as compared to larger sized particles falling the ranges of 250-500 and 500-1000 μm and smaller ones in 63-125 μm size. Similarly, in the case of sugar cane bagasse particles in the range of again 45-63 μm size range gave better sorption capacity as compared to the bigger size ranges indicated for rice husk (Fig. 7). In general, surface area of sorption and intimacy of contact increases with decrease in size the highest surface areas measured being 0.304 and 0.152 m<sup>2</sup> g<sup>-1</sup> for rice husk and sugarcane bagasse, respectively.

**Mechanism of sorption:** The mechanism of sorption for the raw and modified forms of the rice husk and sugar

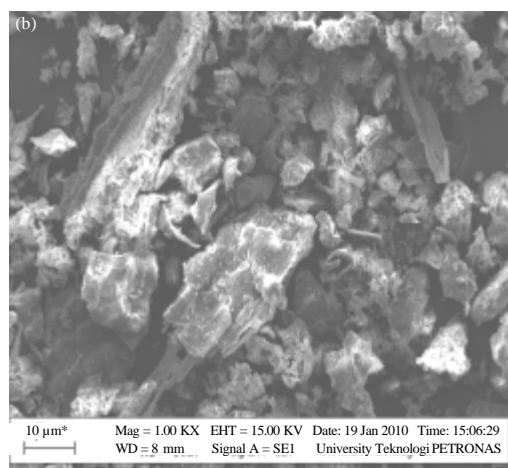
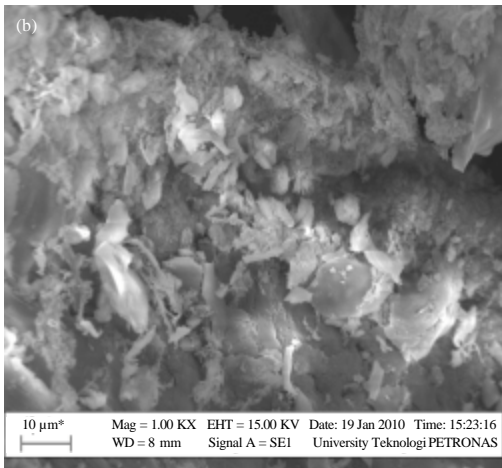
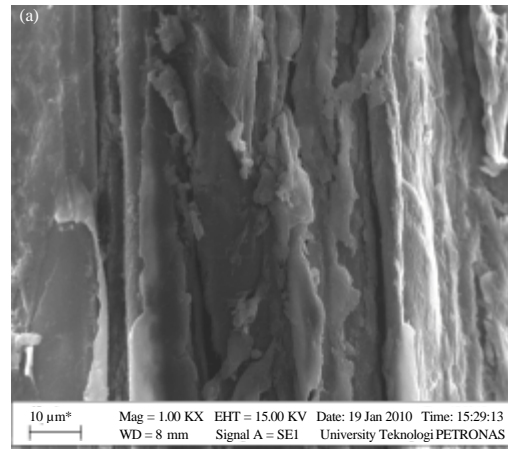
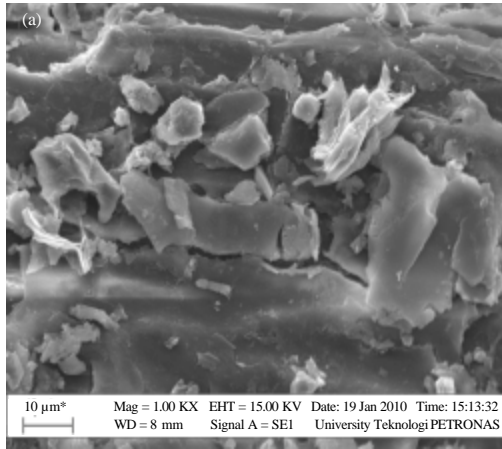


Fig. 5: Scanning Electron Microscope (SEM) image of (a) raw rice husk and (b) rice husk ash

Fig. 6: Scanning Electron Microscope (SEM) image of (a) raw sugarcane bagasse and (b) sugarcane bagasse ash

cane bagasse is linked to the role played by the essential stretching functional groups like Hydroxyl (-OH), Carboxylic acid (-COOH), carbonyl (C=O), C-H, Si-O-Si and Si-OH and other aromatic and phenolic groups existing in the sorbents. Such functional groups can be increased in concentration and/or can be created by the action of the chemical modifiers used in the study. For instance, sodium hydroxide and sulfuric acid decrease or remove low molecular weight lignin compounds which in turn increase the concentration of (-OH) and (-COOH) groups. The burning of the raw rice husk and sugarcane bagasse into ash increases the concentration of Si-O-Si and Si-OH which are believed to play great role in metal removal (Fig. 8). This has been observed in the Fourier transform infrared spectroscopic peaks produced for the

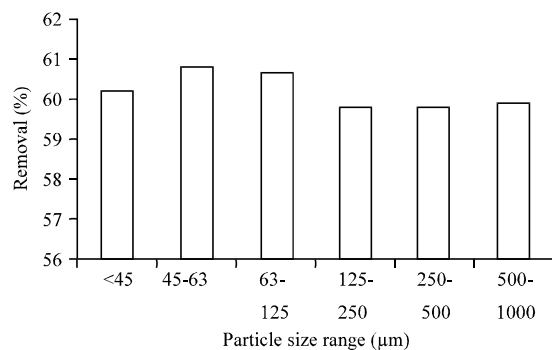


Fig. 7: Impact of particle size on lead sorption capacity of Rice husk and sugarcane bagasse

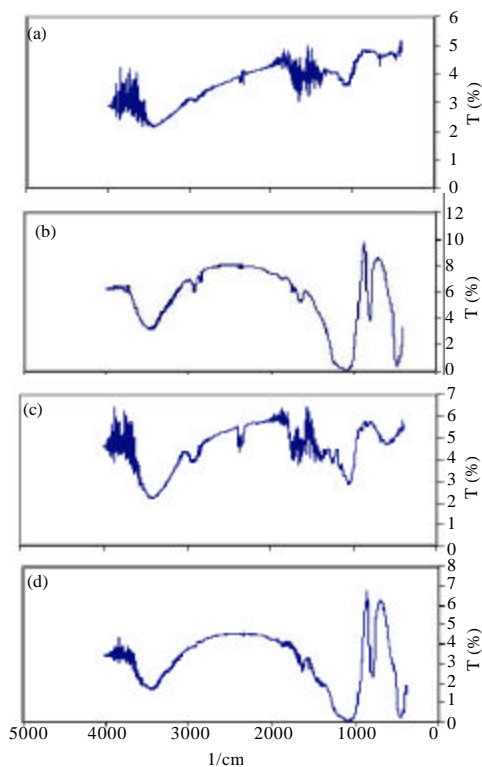


Fig. 8: Fourier transform infrared spectroscopic result of raw and modified rice husk and sugarcane bagasse: (a) Raw Rice Husk; (b) Rice husk ash produced after burning of the husk at 700°C; (c) Raw Sugarcane Bagasse and (d) Sugarcane Bagasse ash burned at 700°C

raw and chemically and thermally modified rice husk and sugarcane bagasse samples tested. Peaks observed to have been involved include those at, 3423 (OH stretching), 2933 (CH<sub>2</sub> stretching), 1650, 1420 (C = O stretching), 1051 (C-O stretching) for sugarcane bagasse and 3400 (OH stretching), 1650 (C = O stretching), 1054 (C-O stretching) for rice husk. In addition, ion exchange plays a significant role in sorption of the metals and this can be deduced from the pH changes that occur after sorption and was proved by comparing the pH at the beginning of the process to the pH after the completion of the sorption tests.

### CONCLUSIONS

In general, chemical modification of rice husk and sugar cane bagasse significantly increases the sorption capacity except the case observed with some chemical

modifiers, a decrease which is probably due to the concentrations used in the study and or the alteration of the ion-exchange environment. Particle size, sorbent concentration and thermal activation are also essential factors that influence the sorption capacity of rice husk and sugarcane bagasse. With the appropriate selection of the chemical modifier and thermal modification condition and other factors mentioned in the study noble low cost sorbents based on rice husk and sugarcane bagasse can be obtained.

### ACKNOWLEDGMENT

The authors gratefully acknowledge Universiti Teknologi PETRONAS for funding this research work.

### REFERENCES

Abdel-Ghani, N.T. and G.A. Elchaghaby, 2007. Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ions from wastewater by adsorption. *Int. J. Environ. Sci. Technol.*, 4: 451-456.

Bailey, S.E., T.J. Olin, R.M. Bricka and D.D. Adrian, 1999. A review of potentially low-cost sorbents for heavy metals. *Water Res.*, 33: 2469-2479.

Davis, T.A., B. Volesky and A. Mucci, 2003. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res.*, 37: 4311-4330.

Garg, V.K., M. Bansal, U. Garg and D.Singh, 2009. Removal of Cr (VI) from aqueous solutions using pre-consumer processing agricultural waste: A case study of rice husk. *J. Hazard. Mater.*, 162: 312-320.

Kapoor, A. and T. Viraraghavan, 1995. Fungal biosorption-an alternative treatment option for heavy metal bearing wastewaters. *Biotechnology*, 53: 195-206.

Karnitz, O. Jr., L.V. Gurgel, J.C. de Melo, V.R. Botaro, T.M. Melo, R.P. de Freitas Gil and L.F. Gil, 2007. Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. *Bioresour. Technol.*, 98: 1291-1297.

Kratochvil, D. and B. Volesky, 1998. Advances in the biosorption of heavy metals. *Trends Biotechnol.*, 16: 291-300.

Kumar, U. and M. Bandyopadhyay, 2006. Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresour. Technol.*, 97: 104-109.

Malik, A., 2004. Metal bioremediation through growing cells. *Environ. Int.*, 30: 261-278.

Ngah, W.S.W. and M.A.K.M. Hanafiah, 2008. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresour. Technol.*, 99: 3935-3948.



- Sud, D., G. Mahajan and M.P. Kaur, 2008. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions: A review. *Bioresour. Technol.*, 99: 6017-6027.
- Tsezos, M., 2001. Biosorption of metals. The experience accumulated and the outlook for technology development. *Hydrometallurgy*, 59: 241-243.
- Veglio, F. and F. Beolchini, 1997. Removal of metals by biosorption: A review. *Hydrometallurgy*, 44: 301-316.
- Volesky, B., 1990. Biosorption by Fungal Biomass. In: *Biosorption of Heavy Metals*, Volesky, B., (Ed.). CRC Press, Florida, pp: 140-171.
- Volesky, B. and Z.R. Holan, 1995. Biosorption of heavy metals. *Biotechnol. Prog.*, 11: 235-250.
- Wang, J.L., 2002. *Immobilization Techniques for Biocatalysts and Water Pollution Control*. Science Press, Beijing.
- Wong, K.K., C.K. Lee, K.S. Low and M.J. Haron, 2003a. Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere*, 50: 23-28.
- Wong, K.K., C.K. Lee, K.S. Low and M.J. Haron, 2003b. Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk. *Process Biochem.*, 39: 437-445.