UTILIZATION OF UNTREATED AND TREATED RICE HUSK AS ADSORBENTS FOR LEAD REMOVAL FROM WASTEWATER

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Abstract: Lead contamination in wastewater from industries has been increasing progressively in many countries including the Philippines. Adsorption is the most promising technology for heavy metals removing from wastewater by using agricultural waste and by-product such as rice husk. Unmodified and modified rice husk have been evaluated as their ability to bind with metal ions. In this study, four characterizations of raw rice husk have been conducted. The specific surface area and pore size distribution by Particle Size Analyzer (PSA), the morphological characteristics by Scanning Electron Microscope (SEM), the functional group present in the rice husk by Fourier Transform Infrared (FTIR) spectroscopy and the pH at point of zero charge by drift test following the method conducted by Ferro-Garcia (1998). It was found that Langmuir surface area of raw rice husk is 2.232 m^2/g. The result of Scanning Electron Microscopy (SEM) also shows that rice husk is a porous material. Rice husk contains of –OH functional group that can bind with metal ions. Following the pH drift tests, the raw rice husk is almost neutral (pH_{PZC} = 6.9). To be able to enhance the sorption capacity of rice husk in metals removing from waste water, acid treatment should be done. This shows that rice husk can be used as adsorbent for heavy metal ions removing from wastewater.

Key Words: rice husk; lead; adsorption; agricultural waste; metal ions

1. INTRODUCTION

Wastewater is being release every day from industries and municipalities to the environment. It contains different toxic pollutants such as organic materials, pesticides, radioactivity and heavy metals in which concentration vary significantly depending on place and time of discharge. Among these pollutants, heavy metals have become one of the most important environmental problems (El-Shafey, 2010) and become a serious concern of scientists, engineers and government authorities (Isa et al., 2010). Lead is a kind of harmful and toxic heavy metal which is used in many industrial processes such as storage battery from manufacturing, printing, pigments, fuels, photographic materials and explosive manufacturing (Aksu & Kustal, 1991).

This pollutant poses a big threat to the environment through its accumulation in the food chain and its persistence in nature.

In the Philippines, lead pollution in water has been increasing progressively. From the Department of Environment and Natural Resources (DENR) Administrative Order 35 of 1990 regulate the allowable of lead concentration in the effluent from old and existing industries is 0.05 ppm (mg/L). Moreover, the current World Health Organization (WHO) drinking water standard for lead (II) is only 0.01 mg/L and the allowable of lead in wastewater set by Environmental Protection Agency (EPA) is 0.05 mg/L. Blacksmith Institute, an international non-for-profit organization dedicated to solve pollution problem, has reported that Marilao River, located in the province of Bulacan, in the Philippines has caused environmental degradation and numerous public health problems because of heavy metal pollution from the discharge of industrial wastewater. As a result, the Marilao River became the subject of two Greenpeace reports in 1996 and again in 2003 about lead contamination. Also, effluent samples taken from a discharge canal of the Philippine Recyclers, Incorporated (PRI) had lead levels of 190 ppm or 3,800 times higher than the 0.05 mg/L standard set for lead in effluent from old and existing industries.

To curtail heavy metal pollution problems, some various techniques for wastewater treatment have been developed through decades including coagulation, chemical precipitation, membrane separation, reverse osmosis, solvent extraction, ion exchange, filtration, and adsorption by activated carbon. Among these methods, adsorption by activated carbon is widely used as an effective adsorbent in many applications but metal ions removal by activated carbon is relatively expensive. Hence there is a need to search for the low cost adsorbent. Rice husk an abundant agricultural waste material generated in rice producing countries is found to be capable of removing heavy metals (Luo et al., 2011) and can be considered as an efficient and low-cost adsorbent for heavy metals.

Rice husk is a major by-product of the rice milling industry that accounts for 20-25% of its weight (Mohan & Sreelakshmi, 2008). In the Philippines, the annual rice production is of more than 16 million metric tons in 2011. Unmodified rice husks have been examined and discovered for its ability to bind metal ions (Zaifang et al., 2011) while various modifications on rice husks have also been reported in order to enhance sorption capacities for metals ions and other pollutant (Kumar & Bandyopadhyay, 2006). Since there is very few researches involved in the utilization of untreated and treated rice husk as adsorbent for heavy metals removal in fixed-bed column. This study will explore more on the potential of these adsorbents to treat the wastewater using fixed bed column, where the removal of lead ions was the main focus.

2. METHODOLOGY

Materials

The main raw material that used in this study is rice husk, Agusan (RC66) variety which was obtained from ST. CATHERINE, local rice mill, located in Bagac Bataan, Philippines. First rice husks were washed thoroughly 3 to 5 times with tap water and continued with distilled water to remove the adhering dirt particles and impurities. This process of washing was repeated until there has no visual indication of dirt in the washed water. After which rice husk was dried in an oven at 105^{o}C until dry. The cleaned and dried rice husk was then stored in air tight container.

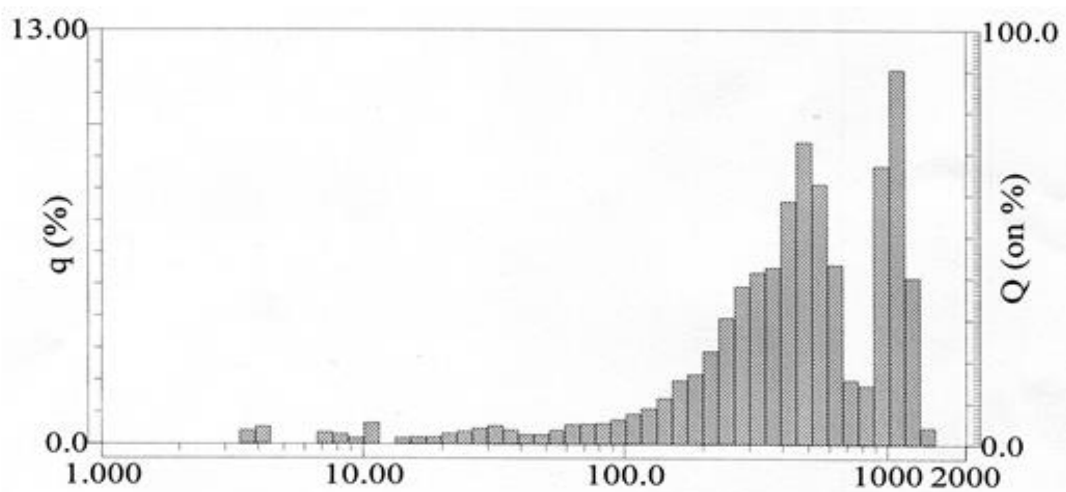
Characterization of rice husk

The specific surface area and particle size distribution of rice husk were characterized by Particle Size Analyzer (PSA) using Nova Station A. The morphological characterization of rice husk was determined by Scanning Electron Microscope (SEM) in order to verify the presence of porosity. The surface functional groups present in the adsorbents were characterized using a Fourier Transform Infrared (FTIR) Spectroscopy (TENSOR37). All these three analysis are done at Ho Chi Minh City University of technology, Vietnam. The pH at point of zero charge of rice husk was also characterized using the drift test following the procedure conducted by Ferro-Garcia (1998). This was done at STRC, De La Salle University.

3. RESULT AND DISCUSSION

Particle size Analyzer (PSA)

The analysis of particle size distribution of raw rice husk was presented in Figure 1.



Particle size (µm)

Figure1: Particle size distribution of raw rice husk

From the figure the particle size distribution of raw rice husk between 3.905 and 1531.914 µm is broadened with the two maxima at 517.20 and 1167.725 µm. From BET characterization of rice husk, the Langmuir surface area of rice husk is 2.232 m^2/g. This value of surface area indicates that rice husk is porous.

Scanning Electron Microscope (SEM) image

The SEM image of raw rice husk with magnification of 45x, 250x, 500x and 1000x was shown in the Figure 2. The bar in the figures indicates the magnification that was represented in µm. The figure revealed that the raw rice husk is a porous adsorbent that can be used for the removal of heavy metal from wastewater such as lead.

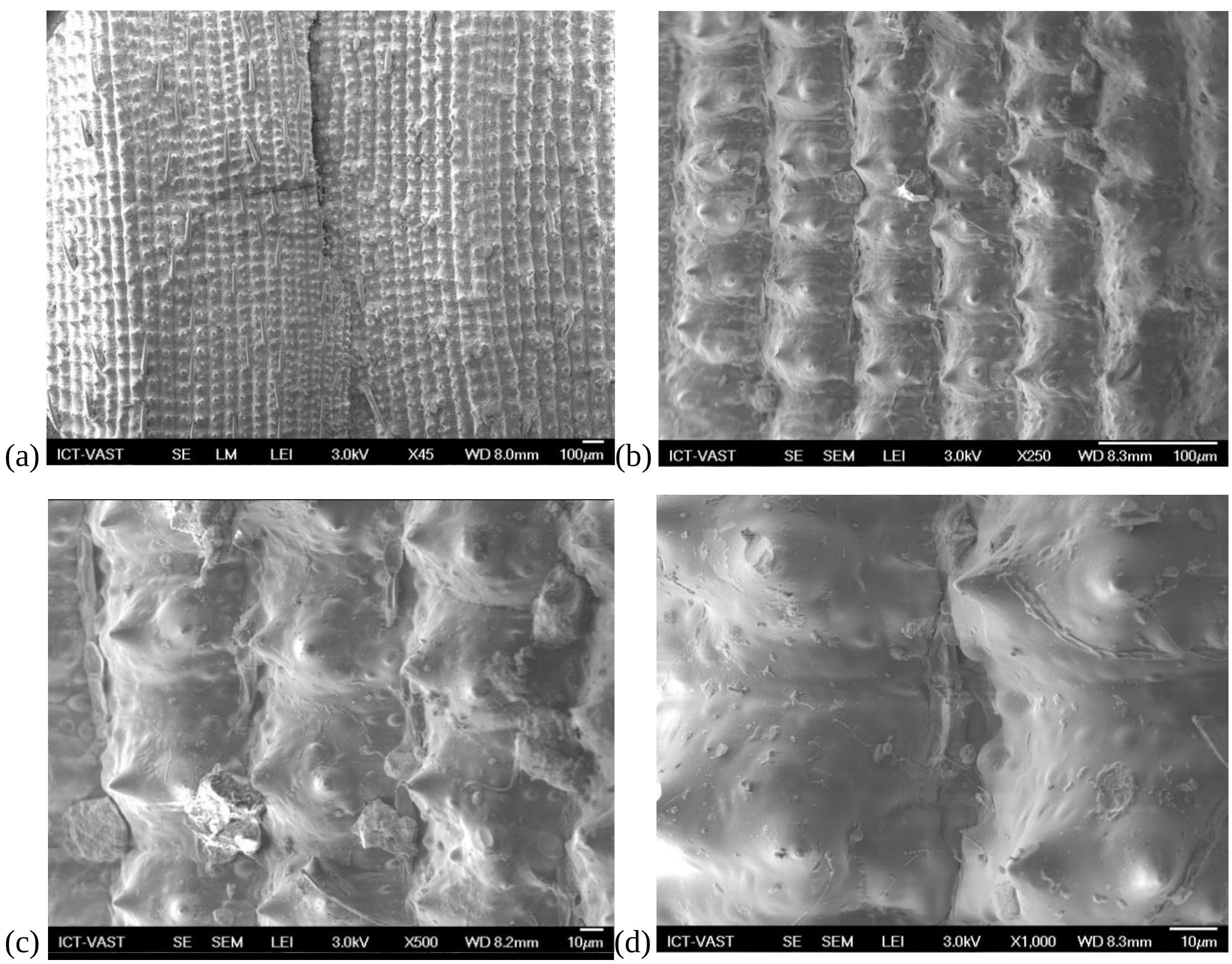
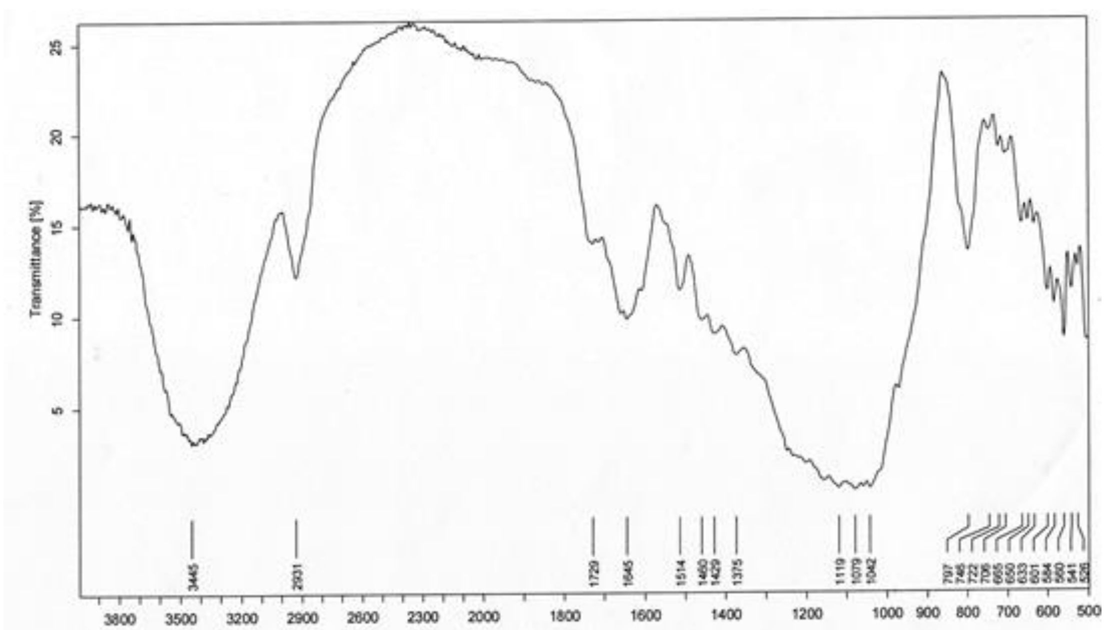


Figure 2: SEM image of raw rice husk (a) 45x, (b) 250x, (c) 500x, (d) 1000x

Fourier Transform Infrared (FTIR) Spectrophotometer

The result of FTIR analysis of raw rice husk was shown in Figure 3. The spectra are recorded between 4000 and 500 cm^{-1}. Rice husk contains of cellulose, hemicellulose, lignin and waxes that most likely consist of alkene, esters, aromatics, ketones and alcohols with oxygen containing different functional groups. From the spectra of raw rice husk presented in Figure 3, the functional group of -OH was presented at the broad band of 3445 cm^{-1}, C-H groups was appeared at the broad band of 2931 cm^{-1} and C=O groups was appeared at 1729 cm^{-1} (Syafri et al., 2011). The broad band appeared at 1460 cm^{-1} and 1042 cm^{-1} ascribed the bending vibration of C=O, $-CH_2$ and $–CH_3$, respectively (Luo et al., 2011). The vibration of C=C (water absorbed) at 1680-1600 cm^{-1}, C=C stretch (aromatic rings from lignin) at 1600-1475 cm^{-1}, C-O-H bending (ester) at 1450-1375 cm^{-1}, C-O stretch (ester) at 1300-1000 cm^{-1}, C-H bending at 900-690 cm^{-1} and C-C stretch at 700-400 cm^{-1} (Syafri et al., 2011 & Ang et al., 2012).



Wavenumber (cm^{-1})

Figure 3: FTIR spectra of raw rice husk

pH at point of zero charge

The pH at point of zero charge (pH_{PZC}) is the pH where the absolute charge on the surface is zero. This characterization procedure is normally implemented for studies which involve the adsorption of heavy metal that occurs significantly in the acidic environment. From Figure 4, the result of point of zero charge of raw rice husk is at pH=6.9.

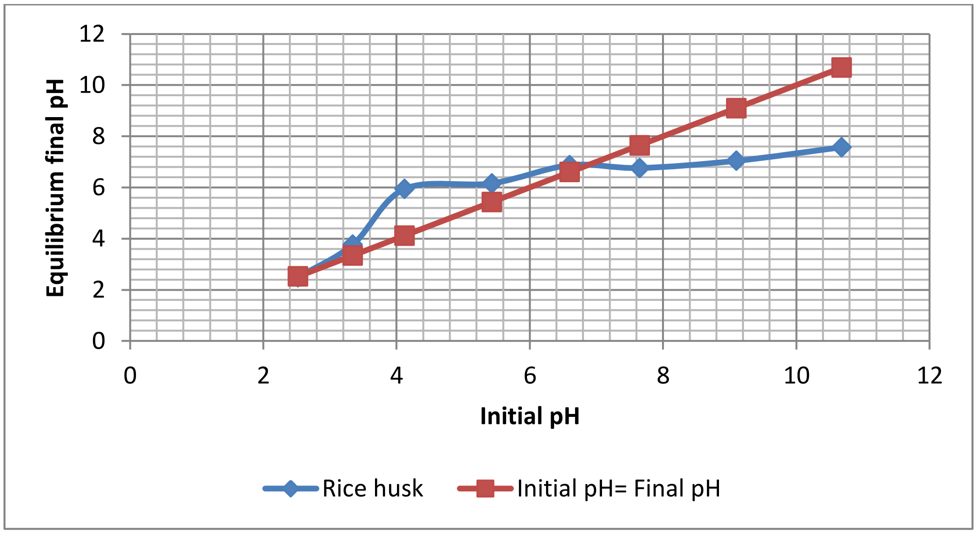


Figure 4: pH of point of zero charge of raw rice husk

4. CONCLUSIONS

Rice husk was found to be a porous material that can be used as adsorbent for heavy metals removal from wastewater. The presence of –OH functional groups in rice husk shows that rice husk has capability in binding with metal ions. The pH at point of zero charge of rice husk is almost at the neutral point so to enhance the capability of rice husk in heavy metal ions removing from wastewater, acid treatment of rice husk should be done.

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