Sorbents derived from lignocellulosic waste materials: characterization and potential removal of surfactants, phenolic compounds, and nutrients from environmental aqueous solutions

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Abstract. Sorbent materials were prepared from two lignocellulosic materials, banana peelings (BP) and rice husks (RH). Scanning Electron Microscopy (SEM) studies revealed that sorbent from BP has a rough surface with structures of no definite shape and size, while RH sorbents showed smooth surface with regular patterns of structures. Fourier Transfrom Infrared (FT-IR) studies also revealed that both sorbents are rich in –OH, –C=O, –CH$_2$ groups and traces of –C-O stretches. Batch sorption experiments were conducted to assess the surfactants, phenols, and nutrient (N and P) removal potential of the prepared sorbent materials under two initial pH conditions (6 and 9) for both surface and effluent water, and two salinity conditions (3 and 33 ppt) for surface water only. In general, both BP and RH derived sorbent materials showed potential in removing surfactants and phenols from surface waters. Removal of surfactants and phenols was observed to be significantly affected by salinity but not by the initial pH level. Sorption of the surfactants to the BP sorbents was observed to be favorable at slightly acidic pH of 6 and high salinity water (33 ppt). Phenol removal by BP and the RH-derived sorbents was not significantly affected by pH changes within the range of common environmental water levels. In contrast, the removal of phenol by both sorbent materials was significantly reduced at higher salinity concentration regardless of the pH level. Lastly, results suggest that the sorbent materials evaluated in this study showed minimal or no potential application as sorbents for reducing nutrient (N and P) concentrations in both surface and effluent waters.

Key Words: adsorption, biomass, pollutants, biosorbents.

Introduction. The pollution of aquatic ecosystems is a widespread problem among developing countries where industrialization, urbanization, and intensive agricultural and aquaculture activities have led to increased disposal of unregulated wastes. These chemical contaminants, primarily of anthropogenic origin, include the heavy metals, wide variety of persistent organic pollutants (POPs), surfactants, and nutrients (nitrogen and phosphorus) (Brar et al 2006).

Surfactants are among the most extensively used chemicals, with important commercial and domestic applications. As such, surfactant contamination of the environment, particularly of urban waterways is inevitable (Krueger et al 1998). Surfactant enters the environment either directly or after treatment in wastewater treatment plants (Alvarez-Munoz et al 2010). They poses threat to aquatic ecosystem, since they are known to be toxic to a number of aquatic organisms (Venhuis & Mehrvar 2004).

Phenols and their derivatives are among the most common and toxicologically important pollutants of aquatic ecosystems since they are harmful to aquatic organisms even at low concentration and considered as potential threat to human health (Davi & Gnudi 1999; US-EPA 2002). Primarily of anthropogenic origin, they enter the aquatic environment through municipal and industrial activities, as well as production and use of
agrochemicals (Michalowicz & Duda 2007). Phenolic compounds (e.g. chlorophenols, nitrophenols, alkylphenols) that are resistant to biodegradation, are an important environmental concern (Davi & Gnudi 1999; Mahvi 2008; Michalowicz & Duda 2007; Okasha & Ibrahim 2010).

Another common pollutant of urban waters are nitrogen and phosphorus. They are nutrients that promote plant and algae growth in aquatic environments. At elevated concentrations however, N and P are the primary causes of eutrophication or nutrient-enrichment in surface waters. This in turn results to harmful algal blooms leading to depletion of dissolved oxygen in the aquatic environments, or hypoxia and anoxia. Ultimately, nutrient pollution may lead to ecological imbalances and decrease in aquatic biodiversity (Howarth et al 2000).

Various processes – physical, chemical and biological, either singly or in combinations are available to treat these wastes. However, most existing physico-chemical methods such as chemical precipitation, ion-exchange, and membrane processes are slowly losing ground due to inherent problems of secondary contamination and expensive operations (Kaewsarn et al 2008; Tamura et al 2010; Okasha & Ibrahim 2010). This created interest in developing sorbent-based waste removal techniques. The use of sorbent materials has been shown to be an effective method for the removal pollutants from aqueous solutions (Mukherjee et al 2007). Activated carbon is the most widely used sorbent materials because it has excellent adsorption efficiency for the organic compound (Velmurugan et al 2011; Mukherjee et al 2007). Nevertheless, commercially available activated carbon is expensive (Annadurai et al 2002).

Adsorbents based on plant-derived materials have been widely studied to develop cost-efficient sorbent materials for the removal of different chemical pollutants. The application of biosorbents on heavy metal removal is already well-documented. Most of these studies rely on the inherent capacity of the sorbent material to adsorb heavy metals through direct interactions between the metals and the surface functional groups on the biosorbent materials (Kaewsarn et al 2008; Memon et al 2008). On the other hand, the use of biosorbents for organic pollutants and nutrients are less straightforward and therefore has received considerably less attention (Moreno-Castilla 2004; Eberhardt & Min 2008; Taffarel & Rubio 2010).

Banana peelings and rice husks are common agricultural by-products particularly in developing countries where banana and rice are heavily consumed (FAO 2009). Since both of these agricultural products are greatly consumed, significant amount banana peelings and rice husks are generated as solid wastes every day. Because of their availability and abundance, and inherent chemical characteristics, both banana peelings and rice husks are widely studied for their potential to adsorb a wide variety of chemical species, from various heavy metals (Kaewsarn et al 2008; Memon et al 2008; Asrari et al 2010), to some organic compounds (Achak et al 2009; Abdelwahab et al 2005).

This study investigates the potential of common lignocellulosic wastes for the removal of ubiquitous environmental water pollutants. Sorbents were prepared from untreated banana peelings and rice husks. Physicochemical properties of the sorbents prepared were also investigated. Finally, batch sorption experiments were done to assess their potential for the removal of surfactants, phenols, and nutrients from environmental water.

**Material and Method.** This study was done from November 2011 to November 2012. All of the organic solvents and salts used in this study were purchased from Scharlau Chemie. Sodium dodecylsulfate (SDS) was purchased from Sigma-Aldrich. All chemicals used were at least of analytical grade, and no further purification was performed before using.

**Sorbent materials.** The sorbent materials used were banana peels (BP) and rice husks (RH). BP were collected as waste from peeled banana purchased at the local public market (Miagao, Iloilo, Philippines) while the RH were collected from Dumapig Milling Corporation (Pontevedra, Capiz, Philippines). The sorbents materials were washed immediately with distilled water after acquisition, and oven-dried. The dried clean
samples were then osterized and sieved (600 μm). Finally, the samples were washed several times with distilled water, oven-dried (100°C), and kept inside desiccators before use.

**Sorbent properties.** Scanning electron microscope (SEM) imaging was done at the Southeast Asian Fisheries Development Center – Aquaculture Department (SEAFDEC-AQD) using a JEOL JSM-5510 scanning microscope. Varying magnifications were used to investigate and compare the structures and surface characteristics of the two sorbents. Fourier Transform Infrared (FT-IR) analyses of the prepared sorbents were carried out to characterize the surface functional groups present. To obtain the FT-IR spectra, very small amount of sorbents were ground and mixed with KBr, and then pressed into pellets. The Infrared spectra of the sorbents were measured using Avatar 330 FT-IR Thermo Nicolet.

**Environmental water samples.** Water samples were taken from two different locations of Iloilo River Estuary. During low tide, a bulk of water sample with a salinity level of 3 ppt was taken upstream of the river. Another bulk of sample was collected downstream of the river during high tide where the salinity was at 33 ppt. A bulk of sample was also taken from an effluent water source discharging directly on the estuary. Salinities of the surface water samples were monitored using a portable refractometer.

**Batch sorption experiments.** The sorption of surfactant, phenol, and nutrients (N and P) were investigated using batch sorption experiments. Experiments on both surface and effluent waters were done at two initial pH conditions (6 and 9). In addition, sorption studies on surface water samples were also evaluated at two salinity conditions (3 ppt and 33 ppt). Four separate water samples were spiked with SDS, phenol, ammonium nitrate (NH₄NO₃), potassium biphosphate (K₂HPO₄), to make an initial nominal concentration of 50 mg-SDS L⁻¹, 10 mg-phenol L⁻¹, 100 mg-N L⁻¹, and 10 mg-P L⁻¹ respectively. In each treatment, 250 mg of the prepared sorbent materials was added to 100 mL of spiked water sample. The mixtures were then agitated using a mechanical shaker at a rate of 60 rpm for 12 hours at laboratory temperature. Finally, the mixtures were then filtered, and the amount of phenols (US-EPA 1983), SDS,nitrogen (as nitrate-nitrite), and phosphorus (as phosphate) were extracted and analyzed using standard methods (APHA-AWWA 1999; AOAC 2006). Percent (%) removals were then calculated accordingly. All treatments were done in triplicate, and the average ± standard deviation values were reported. Controls treatments (no sorbent materials added) were also prepared along with the treatments amended with sorbent materials.

**Results and Discussion**

**SEM studies.** The SEM imaging of the unloaded BP sorbents (1500X) shows that the surface of the sorbent is rough, having discrete structures and pores with no definite size and shape (Figure 1.a). In contrast, SEM imaging of RH sorbent at same magnification reveals that the surface of the sorbent is relatively smooth (Figure 1.b). Images of sorbent from RH at lower magnification level (300X) also show regular patterns of grooves and ridges on the surface. These microstructures on the surface of the sorbent materials are proven to facilitate adsorption of various molecules (Bansal et al 2009).
FT-IR studies. Surface functionality of the sorbents materials does not appear to differ between the two lignocellulosic materials, although the BP spectra showed slightly higher absorptions (Figure 2). Both sorbents showed four significant bands, at 1) wave number 3400 cm\(^{-1}\), representing \(-\text{OH}\) groups, 2) at 2920 cm\(^{-1}\) which is assigned to \(-\text{CH}_2\) biopolymers, 3) at 1700 cm\(^{-1}\) attributed to C=O stretches, and 4) at 1250 cm\(^{-1}\) and 1050 cm\(^{-1}\), indicative of C-O stretches from glycosidic linkages of polysaccharides (Adapa et al 2011; Xu et al 2013; Nguyen et al 2008). These observed functional groups have been reported to be characteristic chemical groups of lignocellulosic materials, including the processed ones, such as biochars and the activated carbons.
**Surfactant removal.** Two salinity conditions were considered for the surface water samples, 3 and 33 ppt. Salinity conditions were varied by collecting samples from upstream part of the river (low salinity) and downstream part of the river (high salinity). Sorbents from RH showed higher removal of surfactants from the surface water samples (Figure 3). The pH difference does not significantly affect the removal of surfactants by either sorbents (RH or BP). However, an increase in surfactant removal, was observed at the higher salinity condition. Similar observation was reported by Mi-na et al (2006) in the removal of sodium dodecylbenzenesulfonate (SDBS) surfactant from aqueous solution using chromium-containing leather waste as the sorbent. Overall, the higher surfactant removal in high salinity (33 ppt) water may be due to the possible formation of electrical double layer of the dissolved NaCl in the solution. The electrical double layer results from the unequal distribution of electrical charges at the interface between surfactant and the sorbents as previously described by Mi-na et al (2006) and Yang et al (2004). It has been shown that with the increase in salinity (i.e. NaCl concentration), the electrical double layer on the surface of the sorbent may compress and the electrostatic repulsion between the adsorbed surfactant species decreases, resulting in increased adsorption capacity of the sorbent material (Yang et al 2004).

Another important mechanism for surfactant adsorption is the hydrophobic interaction between the alkyl hydrocarbon chain of the surfactant and the hydrophobic sites on a sorbent material (Taffarell & Rubio 2010). Previous studies described the adsorption of surfactant on the surface of cation surfactant-modified natural zeolite, where the pH of the solution is not a significant factor in the sorption process (Taffarell & Rubio 2010). Moreover, surface morphology are very different (Figure 1), which could also be factor in the differences in sorption efficiency between the two sorbents.

![Figure 3. Removal of SDS from contaminated surface water (SW) and effluent water (EW) under varying experimental conditions (pH 6 and 9; salinity levels 3 ppt (SW3) and 33 ppt (SW33)). Values are mean ± sd; n = 3.](image)

**Phenol removal.** In all treatment conditions, sorbents from BP showed higher removal of phenol than the RH-derived sorbent material (Figure 4). The highest removal of phenol (40.14%) by sorbents derived from BP was observed at lower pH (6) and lower salinity condition (3 ppt). Also, while pH changes do not appear to significantly affect the removal of phenols, the removal of phenol by both sorbent material from surface water samples was significantly reduced at higher salinity levels regardless of the pH. This observation appears to be related to the increase in the extent of water adsorption on the surface hydrophilic oxygen groups of sorbents (Arafat et al 1999). Formation of water clusters on the surface of sorbents hinders the access of phenol to the active sites of the sorbents surface. The effects of water adsorption increase with salinity because of the ion-exchange between H⁺ of −COO−H and −O−H groups of the sorbents, and the salt cations (e.g. Na⁺, and K⁺) (Arafat et al 1999).
In addition, adsorption of phenolic compounds has been reported as partly physical and partly chemical (Moreno-Castilla 2004). In terms of physical adsorption, adsorption capacity will greatly depend on the access of the organic molecule to the inner surface of the adsorbents, which is a function of size. It has been shown that small molecules like phenols access the micropores (Moreno-Castilla 2004). As such, if the adsorption is governed by non-electrostatic chemical interaction, which is the likely scenario in the present study, adsorption of the phenol is reduced, when accessibility to micropore system is reduced. Increasing ionic strength of the solution, can result in screening effect as a consequence by the higher salt concentration in high salinity samples (Moreno-Castilla 2004).

Given that the surface functionalities of the two sorbent materials do not differ significantly (Figure 2), the observed differences could be a physically-driven adsorption. Scanning electron microscope (SEM) images of the two sorbent materials, revealed very different surface morphologies (Figure 1). The BP-derived sorbent shows a clearly visible micropores, not seen in the close inspection of RH-derived sorbent, which can be accessed by the phenol molecules (Moreno-Castilla 2004).

The results of the present study is also in agreement with findings of adsorption studies for phenol removal from aqueous solution using other carbonaceous materials (Rengaraj et al 2002; Mukherjee et al 2007). Adsorption studies for phenol removal from aqueous solution on activated palm seed coat carbon (PSCC) reported that percent removal remained constant over the pH range 4-9 (Rengaraj et al 2002). Overall, findings from the present study suggest that water pH will not significantly affect sorption of the BP- and RH-derived sorbents, at the environmentally realistic conditions (i.e pH 6.5-8.5).

![Figure 4. Removal of phenol from contaminated surface water (SW) and effluent water (EW) under varying experimental conditions (pH 6 and 9; salinity levels 3 ppt (SW3) and 33 ppt (SW33)). Values are mean ± sd; n = 3.](image)

**Phosphorus (phosphate) removal.** Both sorbents showed very low phosphate removal at low pH condition. In fact, actual values even suggest that the sorbents released a small amount of phosphate back into the solution (Figure 5). This is in good agreement to literatures (Eberhardt et al 2006; Krishnan & Haridas 2008) and the fact that most lignocellulose-based sorbents have highly negative zeta potential (Eberhardt et al 2006; Yao et al 2011). On the other hand, removals of phosphate at high pH condition were very high for both sorbents. However, the reductions of phosphate were even higher in the control treatments. This means that the reduction of phosphate could be explained by mechanisms other than phosphate adsorption on the sorbent materials. One possible explanation for this result is the precipitation of phosphate from the solution as hydroxyapatite (Ca$_5$(PO$_4$)$_3$OH), which is highly favored at elevated pH conditions (Ferguson et al 1973; Eberhardt et al 2006). This phenomenon is further supported by the observation of insoluble matters in the solution after the treatment.
Nitrogen (nitrate-nitrite) removal. Though amendments with the sorbent materials showed significant removal of nitrogen from the solutions, control treatments even showed higher reductions. This suggests that the removal of nitrogen from the solutions cannot be associated to its adsorption on the sorbent materials. The lack of adsorption could still be explained by the fact that the zeta potentials of lignocellulosic sorbents are highly negative (Eberhardt et al 2006; Yao et al 2011). The removal of nitrogen is therefore associated to other factors and matrix effects that were not covered on this study.

Conclusions. Based on the partial characterization of the physicochemical properties of the sorbents derived from BP and RH, as well as the preliminary evaluation of surfactant, phenols, and nutrient sorption, it is evident that 1) surface morphology of the of the two sorbent materials are very different and could be a factor in the differences in their sorption efficiency on pollutants under study, 2) surface functionality of the sorbents does not appear to differ, although BP showed slightly higher adsorption. In addition, 3) the sorbents showed potential for the removal of phenols and surfactants from contaminated environmental aqueous solution, 4) and the removal of both phenols and surfactants appears to be affected by the salinity of the environmental water, but not of...
the initial pH conditions. 5) Lastly, the potential of both sorbent materials to remove nutrients (N and P) from environmental water is not evident, thus further investigation is recommended.

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