COCOS NUCIFERA SP. BIOSORPTION OF PHARMACEUTICAL PRODUCTS IN WASTEWATERS: A PRELIMINARY ASSESSMENT

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ABSTRACT

This study aimed to establish the adsorption characteristics of coconut husks, in the form of activated carbon in the removal of pharmaceutical products. Equilibrium test was conducted at varying initial concentrations to determine the effect as needed for optimum adsorption. The artificially contaminated wastewater was prepared by spiking pharmaceutical products – Ibuprofen and Paracetamol – in distilled water. Coconut husks were chemically activated by soaking in a 0.01M potassium hydroxide solution (KOH), as dehydrating agent at impregnation ratio of 1:1. Then was oven dried for 3-5 hours at 110 ?C, cooled to room temperature and ground using mortar and pestle. Wasterwaster samples with initial concentration ranging from 200-500 ppm were exposed for 24 hours with the activated cocos nucifera biosorbent. Samples were analyzed via Perkin Elmer Lambda 40 UV Visible Spectrophotometer with the maximum wavelength of 273nm and 248nm, respectively. The results of the analysis showed that coconut husk is not effective biosorbent for pharmaceutical products, particularly Ibuprofen with the adsorption percentage ranging from -14.5% to 14% and relatively low effectiveness in Paracetamol with percentage ranging only from 8% to 38.5%. The equilibrium loading was found to increase as the initial concentration decreases. Although the results displayed a successful process of biosorption of the pharmaceutical residues, that have been tested, especially for Paracetamol, the percentages of adsorption were relatively low as compared to the findings of previous studies. Thus, it cannot be clearly accounted that activated coconut husk is the most appropriate material for the removal of such organic compounds. Moreover, the differences among the concentrations of the samples in the study were limited. This may have impacted the efficiency of the biosorbent to the adsorbate.

Keywords: *Cocos nucifera, activated carbon, pharmaceutical residues, wastewaters, UV visible spectrophotometer*

INTRODUCTION

With its archipelagic nature, water in the Philippines can be derived from various source points such as rainfall, surface waters, i.e. rivers, lakes, and reservoirs, and groundwater resources (Greenpeace, 2007). Accordingly there are 421 river basins, 72 lakes and numerous creeks and streams that make up 86.2% of the total water resources (Phil. Senate Economic Planning Office, 2011). Given such nature, it is ideal to say that the country has an adequate supply of water to provide its sectors but seasonal changes and geographic biases present some logistics problems for the distribution and quality of water (Greenpeace, 2007). For such a country with rich water resources, it is quite ironic that much of the water crisis in the Philippines relates more to lack of quality than lack of quantity (Philippine Senate Economic Planning Office, 2011).Water usage in the Philippines is dominated by the agricultural sector consuming 85.27% of the total followed by the Industrial and domestic sectors at 7.46% and 7.27%, respectively (PEM, 2003; 2004 as cited in Greenpeace, 2007).

Pollution interacts naturally with biological systems. It is currently uncontrolled, penetrating into any biological entity within the range of exposure. The most abundant contaminants include heavy metals, pesticides and other organic compounds which can be toxic to wildlife and humans even in small concentrations. On a yearly basis, it is estimated that 2.41 million tons of hazardous waste are produced (Greenpeace, 2007). In addition, "concern is growing over the contamination of the environment with pharmaceutical residues, among which the non-steroidal anti-inflammatory drugs (NSAIDs) appears to be of the most abundant groups. Their widespread appearance in the aquatic environment is because of their high consumption and their incomplete removal during wastewater treatment." (Kosjek, Heath & Kompare, 2007 p.1379) This means that a need to identify new ways of removing such class of pollutants in wastewater is of importance.

Moreover, "pharmaceuticals are among the most important new classes of environmental pollutants; their occurrence has been reported in natural waters, wastewater, sediments, and sludge" (Fatta-Kassinos,Meric and Nikolaou, 2010 p. 254). For these products are, however, usually do not completely absorbed and metabolized by humans but partially excreted again and their traces reach the water cycle. Pharmaceutical residues found in water are at extremely low concentrations; often lower than was possible (PILLS Project, 2010).

With literature available, other researches (Vieno, Härkki, Tuhkanen and Kronberg, 2007; Dorne, Ragas, Frampton, Spurgeon and Lewis, 2007;PILLS Project, 2010) have identified substances considered as important, that among different countries, similar drugs have been accounted although their concentrations may vary because some pharmaceuticals with a high consumption rate in few areas are not used at all in others. These abovementioned previous researches selected eight substance groups of active pharmaceutical products: analgesics, anesthetics, cytostatics, antibacterials, X-ray contrast media, anticonvulsants, lipid regulators and betablockers.

Removal of such compounds can be accomplished with biosorption. According to Mahmood, Malik and Hussain (2010), "[the] process involves a solid phase (sorbent or biosorbent; usually a biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ion). Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound with different mechanisms. The process continues until equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution." Also, Vijayaraghavan and Yun (2008) stated that it can be defined as the passive uptake of toxicants by inactive biological materials or from such by-products. Biosorption is due to a number of metabolism-independent processes that essentially take place in the cell wall, where the mechanisms responsible for the pollutant uptake will differ according to the biomass type.

While choosing the biomass for biosorption, its origin is a major factor to be taken into account. Fast-growing plants that are specifically cultivated for biosorption purposes (e.g. weeds) can be used as biosorbents (Mahmood, Malik & Husain, 2010). Apart from the microbial sources even agricultural products such as wool, rice, straw, coconut husks, peat moss, exhausted coffee (Dakiky et al. 2002), waste tea (Ahluwalia and Goyal 2005) are used.

The coconut (*Cocos nucifera sp.*), which this study utilized to prove as a suitable biosorbent along products related to it like coir sith and lumber, and some other waste products of processed coconuts like coconut bunch waste (Hameed, Mahmoud & Ahmad 2008), have been cited as possible biosorbent material particularly on cationic and anionic dyes (Etim, Umoren & Eduok, 2012; Salleh, Mahmoud, Karim&Idris, 2011; Rangabhashiyan, Anu & Selvaraju, In Press; Tumlos, Ting, Osorio, Rosario, Ramos, Ulano, Lee & Regalado 2011) and been tested for heavy metals (Sousa, Oliveira, Nogueira & Esposito, 2010) like Cadmium (Pino, Mesquita, Torem& Pinto, 2006) and Pb (II) ions (Singha& Das, 2012). The studies mentioned above have results that show that indeed the coconut is a possible adsorbent----probably an effective one.

Several processes were used to treat the coconut in preparation for adsorbent experiments. This include washing with distilled water and oven drying to 70 degrees Celsius in one study (Hameed, Mahmoud & Ahmad 2008), and sometimes only a minimum of processing like washing, drying and grinding (Salleh, Mahmoud, Karim & Idris, 2011).This paper intends to test one of the principal mechanisms of activated carbon, the adsorption capacities, (DeSilva, 2000), derived from the coconut husks. Activated carbon can be mostly derived from raw material such as wood, petroleum and coconut shells (DeSilva, 2000; Cameron Carbon Incorporated, 2006). Depending on the material, different properties of activated carbon can be made where each can be preferable than the other depending on the usage (DeSilva, 2000; Cameron Carbon Incorporated, 2006). The adsorption performance of activated carbon is affected by several factors like temperature, pH, particle size and flow rate of the contaminant (DeSilva, 2000).

The extent of the study is limited to the attempt of removing environmental water- occurring pharmaceutical residues, specifically analgesics. According to Gale Encyclopedia of Medicine (2008), "Analgesics are those drugs that mainly provide pain relief. The primary classes of analgesics are the narcotics, including additional agents that are chemically based on the morphine molecule but have minimal potential; non-steroidal anti-inflammatory drugs (NSAIDs) including the salicylates; and acetaminophen. Analgesics provide symptomatic relief, but have no effect on the cause, although clearly the NSAIDs, by virtue of their dual activity, may be beneficial in both regards." Figures 1 and 2 show the molecular structure of the most commonly used analgesics.

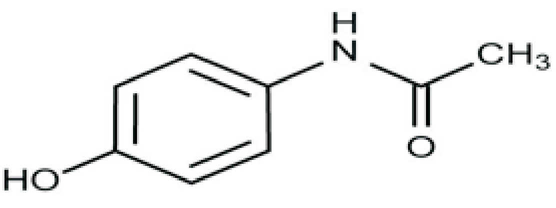

Figure1. Molecular structure of Paracetamol

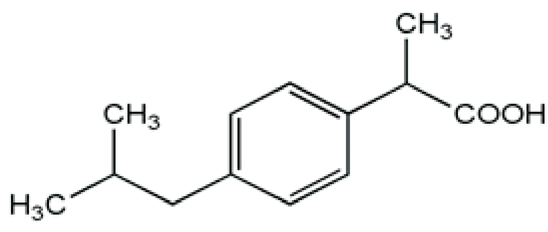

Figure2. Molecular structure of Ibuprofen

The main objective of this study was to establish the sorption characteristics of coconut husks, in the form of activated carbon in the removal of pharmaceutical residues at varying initial concentrations. Specifically, it wanted to determine the effect of initial concentration on the equilibrium needed for satisfactory adsorption.

The current study aimed to prove as well that *Cocos nucifera sp.* (coconut husk) is an effective biosorbent in removing pharmaceutical residues, specifically analgesics such as Paracetamol, and Ibuprofen in environmental waters. Coconut husks served as the main material for the research as well as to test the sorption abilities of the material in high concentrations of toxicants in water. Its significance will bring practical applicability of another method in utilizing such organic substance. Also, it will pave the way of exploring for the extraction or testing of the Philippine waters with the industrial wastes it contains such as pharmaceutical residues, specifically those that are classified to be the most abundant, given a dearth of literature in the country.

While this current study is geared toward the use of coconut husk as an effective biosorbent in the removal of pharmaceutical by-products in the waters of the Philippines. The water to be used is artificially prepared, thus effects of its components that may cause obstructions are not to be considered. The study will be limited to analgesics, specifically, Paracetamol, and ibuprofen; therefore other types of non-steroidal anti-inflammatory drugs (NSAIDs) and other pharmaceutical products are not included for testing. More so, other parameters of adsorption such as the effects of varying pH, varying contact time and varying mass of biosorbent were not tested. More so, the maximum wavelengths used were based from literature available, indicating high applicability in the adsorption of pharmaceutical residues in very low concentrations. The experiment only intended to test its use in varying and relatively high initial concentrations, specifically for Paracetamol.

METHOD AND MATERIALS

Selected Pharmaceuticals

For all lab- and pilot-scale spiking experiments, two relevant pharmaceuticals (Analgesics) have been selected as target and they are as follows; Paracetamol, (NSAIDs) and Ibuprofen.

Preparation of activated coconut husks

As adapted from the study of Din, Hameed and Ahmad (2009), coconut husks were collected from the market. The material was washed with tap water to remove attached impurities. Afterwards, it was boiled using a hot plate for 1.5 hours, with temperature ranging from 100?C to 120?C. An accurate weight of 1.5 kg of produced coconut husks was soaked in a prepared 0.01M potassium hydroxide solution (KOH), as dehydrating agent at impregnation ratio of 1:1. The soaked coconut husks mixture was oven dried for 3-5 hours at 110 ?C, cooled to room temperature and ground using mortar and pestle. The activated carbon was finally kept in air tight closed container.

Artificial Wastewater

Water solution of pharmaceutical compounds, 200, 300 and 500 mg of each studied compound in 1000 mL of distilled water, was spiked.

Equilibrium Test

Equilibrium of the pharmaceuticals adsorption was studied essentially at 30 ?C. To determine the equilibrium, adsorption tests were carried out by adding similar amount of adsorbent to a series of 4-liter PET bottles filled with a 1000 mL solution of either: paracetamol, and ibuprofen (Baccar, Sarrà, Bouzid, Feki & Blánquez, 2012).

Adsorption experiment was conducted through an aeration process by agitating different flasks containing solutions of different concentrations of the analgesics, paracetamol and ibuprofen with the same amounts (approximately 2.5 grams) of the adsorbent, activated carbon of coconut husks for 24 hours sufficient enough to reach equilibrium adsorption maintained at a definite temperature for each. Only the effect of concentration was subjected to study.

UV Visible Spectrophotometer Analysis

The samples prepared were subjected to UV Visible Spectrophotometer Analysis. The analysis was based on the theory that a compound's absorption of light depends on the molecular structure and concentration that the compound has (Sousa, 2009). From this absorption of light, the concentration of the compound on an aqueous sample can be determined. The samples were tested via a Perkin Elmer Lambda 40 UV Visible Spectrophotometer to determine the concentration of pharmaceuticals left on the samples after the 24 hours exposure to the adsorbent, using the maximum wavelength of 248 nm for Paracetamol and 273 nm for ibuprofen.

Adsorption Efficiency

The efficiency of the adsorption was calculated using this equation:

$$\% \, \boldsymbol{adsorption} = \frac{C_i - C_{eq}}{C_i} \times \mathbf{100} \qquad \text{[Eqn. 1]}$$

where:

C_i = initial concentration of the adsorbate (ppm)
C_{eq} = final equilibrium concentration of the adsorbate (ppm)

The equilibrium loading , $q_e(mg\ g^{-1})$, or the amount adsorbed per unit mass of adsorbent was calculated from the following equation:

$$q_e = \frac{V(C_i - C_{eq})}{m} \qquad \text{[Eqn. 2]}$$

where:

C_i = initial equilibrium liquid phase pharmaceutical concentration (mg L^{-1})
C_{eq} = equilibrium liquid phase pharmaceutical concentration (mg L^{-1})
V = volume of the solution in liters
m = mass of the activated carbon used in the experiment in grams.

RESULTS

Table 1: Absorbance values from UV Visible Spectrophotometer

Samples	Conc.(ppm)	UV Vis Absorbance
Ibuprofen	500	0.4029
	300	0.0877
	200	0.0514
Paracetamol	500	0.103
	300	0.1237
	200	0.072

Table 1 shows the absorbance of the two samples based on initial concentration.

Effects of Varying Initial Concentration

The effect of varying the initial concentration in the adsorption of pharmaceutical residues using coconut husk (*Cocos nucifera sp.*) was examined. Table 2 shows the initial concentration, final concentration, equilibrium loading and the percent adsorption of Ibuprofen and Paracetamol. Based from the results of the study, the percent removal of the two pharmaceutical products was found to have different outcomes, positive for Paracetamol and negative for ibuprofen. Thus, implying that coconut husks is not an effective biosorbent of Ibuprofen.

Table 2: Equilibrium loading and percent absorption of analgesics with varying initial concentration

C_i, ppm	C_{eq}, ppm	q, mg/g	% adsorption
Ibuprofen			
500	516	-6.4	-3.2%
300	258	16.8	14%
200	229	11.6	-14.5%
Paracetamol			
500	460	16	8%
300	225	30	25%
200	133	30.8	38.5%

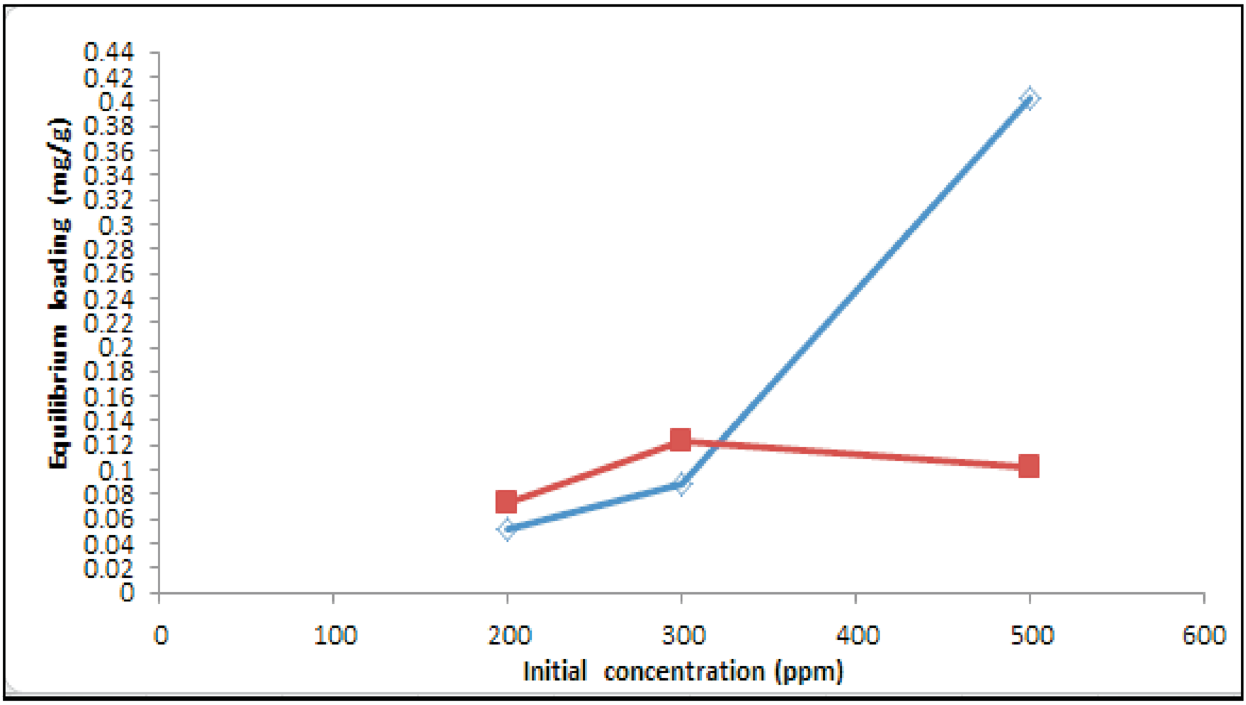

Figure 3. *Equilibrium loading and initial concentration of Ibuprofen and Paracetamol*

DISCUSSION

UV Visible Spectrophotometer is routinely used in Analytical Chemistry for quantitative determinations of solutions with transition metal ions, highly conjugated organic compounds, and biological macromolecules. Highly conjugated organic compounds are seen to be true for carbon compounds with long chains of alternating single and double bonds. This, in turn, makes the contaminants tested qualified, with their respective molecular structure, to undergo the analysis through the UV Visible Spectrophotometer.

The results show that activated coconut husks as biosorbent were found to be not as effective for ibuprofen based on the absorbance displayed upon doing the analysis. This negative result can be better accounted for the reason that the maximum wavelength used for testing the product is practically best suited for the adsorption of Ibuprofen in water but in very low concentrations. On the other hand, it can be drawn out that biosorption of Paracetamol using coconut husk have been effective, although results of the percentage absorption are relatively low.

Seemingly, it can be said that biosorption might have taken place, which may be attributed to the process of biosorption being a method of mass transfer. A driving force is required to achieve transport of mass, which is a concentration gradient in this study. This implies that the greater the difference of concentration, the greater the mass that will be transported. This is supported by the Beer-Lambert's Law, which states that the absorption is proportional to the concentration of absorbing species in the material and its light path (Ingle & Crouch, 1988).

Seemingly with the results of this study, this concept has been contradicted because at least for

Paracetamol, there seem to be a different result: greater the initial concentration, there is a lower percent of absorption. But like any other law, the Beer-Lambert's law has implicit assumptions that are met experimentally. Otherwise there is a possibility of deviations from the law could be observed. Also under certain circumstances, non-linearity of relationship might be seen (Mehta, 2012). Three categories of deviation from the law are known and they are as follows; a) Real deviations or the limits of the law itself that applies for solutions that are at relatively high concentrations for a possible shift in absorption wavelength of the analyte be present since solute molecules may behave differently and in turn affect the solution; b) Chemical deviations, these occur due to chemical phenomenon involving the analyte molecules due to association, dissociation and interaction with the solvent to produce a product with different absorption characteristics; c) Instrument deviations that occur due to how absorbance measurements were made (Mehta, 2012). Instrument deviation may be accounted for as well to the fact that, the spectrum (UV Visible Spectrophotometer) alone is not, however, a specific test for any given sample (Misra & Dubinskii, 2002). A clearer representation of the process of biosorption of the analgesics is depicted in Figure 4.

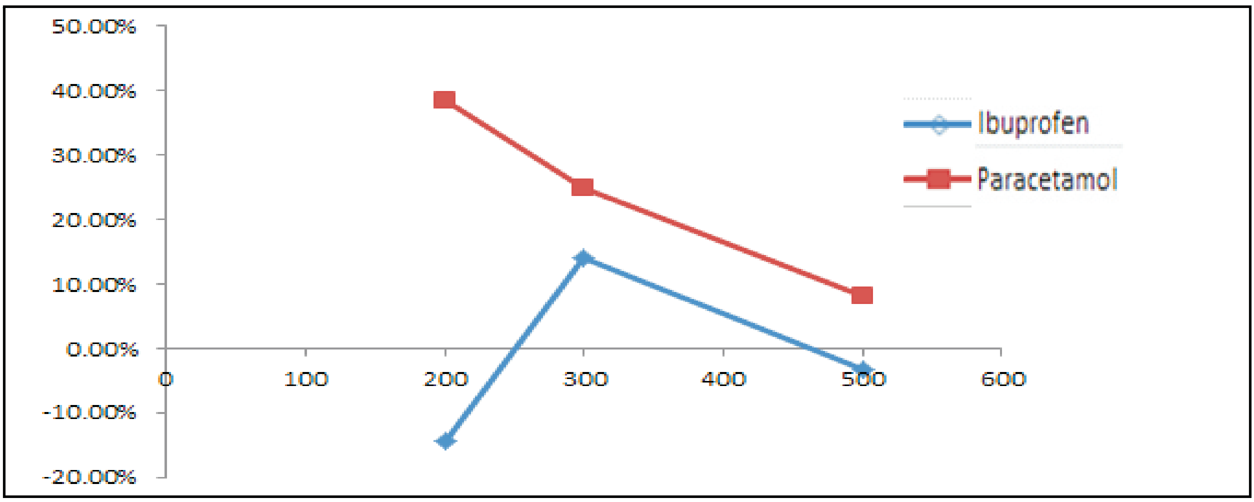

Figure4. *Percentage absorption of analgesics*

Additionally, activated carbon made from coconut husks is considered to be more effective than those obtained from other resources mainly because activated coconut husks exhibit extensive micropores structure (Cameron Carbon Incorporated, 2006) but the material for such sorption process may provide a clear cut notion that coconut husks are not much suitable for the biosorption of pharmaceutical residues in waste waters of high concentrations.

CONCLUSION

Although the results displayed a successful process of biosorption of the pharmaceutical residues that have been tested, especially for Paracetamol, the percentages of adsorption were relatively low as compared to the findings of previous studies. Thus, it cannot be clearly accounted that activated coconut husk is the most appropriate material for the removal of such organic compounds. Moreover, the differences among the concentrations of the samples in the study were limited. This may have impacted the efficiency of the biosorbent to the adsorbate.

RECOMMENDATION

As future direction of researchers on pharmaceutical residues, it is recommended that low concentrations of pharmaceuticals be used which may improve the results, since it is reported that these organic compounds are usually found in waste waters in low concentration.

The use of other analgesics or other pharmaceutical drugs is also suggested, as well as consideration of the effect of other adsorption properties like pH, amount of biosorbent and contact time. Increasing the concentration gradient (differences in the concentration) may also enhance the results. Furthermore, recommendations on the use of other parts of coconuts instead of husks, as well as other low-cost materials must be considered for future studies.

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