A RESEARCH PROJECT REMOVING HEAVY METALS FROM WASTEWATER OF SMALL-SCALE GOLD MINERS OF CAMARINES NORTE (PHILIPPINES) USING COCO-PEAT AS SORBENT MATERIAL

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Abstract

This paper discusses the research project entitled "Development and Testing of Coco-Peat as a Sorbent Material in a Filter Bed". It is a three-year project, commencing in June 2009, and is part of the Better Mine Research Program funded by the Department of Science and Technology (DOST) through the Engineering Research Development for Technology (ERDT) program. The Better Mine program seeks to address the various problems facing the small scale mining industry in the Philippines. One of the major problems facing the mining industry is the treatment of its wastewater which contains heavy metals such as mercury which is used in the amalgamation process. This particular research project examined the possibility of using a locally abundant material and cheap material such as the coco-peat as sorbent for the heavy metals. Results show that coco-peat is a good sorbent material.

Keywords: Coco-Peat, Heavy Metals, Mining, Sorption

Small Scale Mining and Its Impact on Water Quality

The Philippines is blessed with rich mineral resources. The minerals are being mined by both large and small-scale companies. There are many environmental problems associated with mining, such as the release of toxic heavy metals in its wastewater. Large scale companies are able to afford to install treatment plants and tailings dams to manage the wastewater prior to discharge. However, the small scale miners lack the technological know-how as well as the financial resources to install a wastewater treatment plant other than a sedimentation tank.

In places where there are no treatment plants, the wastewater is discharged directly to the receiving bodies of water. In the Philippines, one small-scale mining community is the gold-rich village of Gumaus in Paracale, Camarines Norte. Based on the water quality analysis from the samples from Gumaus River, the impact of mining in the area is evident. Although the parameters monitored were limited only to heavy metals regulated by the Philippine Drinking Water Standards, the contamination revealed from the results of the sample analysis cannot be neglected. Levels of mercury, lead, cadmium and barium are elevated (Annual Report, 2012).

The impacts of these heavy metals to the environment and to public health is well known and widely reported in literature. It is to respond to this situation that a research program to treat wastewater from mine wastewater was conceptualized. A low-cost and low-maintenance system needs to be developed which can be used by the target users.

Being an agricultural country, the Philippines also produces large amounts of agricultural wastes which have been proven to be good sorbent materials. One such agricultural waste that can be used for this purpose is coco-peat. Coco peat is a waste material from coco husk and is produced as a powdery, dusty material when decorticating the husk to produce coco fiber. Currently, its main use is as a soil conditioner. Statistics show that the production of coconut in the Philippines is increasing from 11,941,960 metric tons in 1990 to 14,824,585 metric tons in 2005. This increase in the production of coconuts also means an increase in the amount of potential filter medium, which would otherwise end up as additional wastes generated. Thus, using coco-peat will not only solve the environmental problem, but would also add another value to the material.

The Better Mine Program under the ERDT

Funded by the Department of Science and Technology (DOST) – Engineering Research and Development for Technology (ERDT), the Better Mine Program consists of seven projects with various thrusts with a common goal of developing technologies to be utilized by the small-scale miners.

Research Components

The research project described in this paper is one of these projects under the Better Mine Program. Entitled "Development and Testing of a coco-peat filter bed as sorbent material", the project has a duration of three years commencing in June 2009. The following sections briefly discuss the outputs of the research projects.

Characterization of Coco-Peat

Coco peat is the by-product material in the extraction of fibers from the coconut husks. It can be described as composite material made of short spongy fibers and dust. It is the binding material of the coconut fibers and makes up approximately 70% of the coconut husk. It is also called coconut coir dust, coconut coir pith, coir waste, or fiber dust.

Coco peat is an agricultural waste material from the coconut industry in the Philippines. It is currently under-utilized in the country, commonly used only as soil conditioner. Most of the material ends up in high mounds within the perimeters of decortication plants.

The effective size, d_{10}, was found to be 0.23 mm while the corresponding d_{30} and d_{60} are 0.39 mm and 0.69 mm, respectively. The values obtained for the coefficients of uniformity and gradation were 3.00 and 0.96, respectively. This indicates that the coco peat used in the experiment is well-graded. Furthermore, most of the coco peat particles, comprising more than 70% by mass, have diameters ranging from 0.15 mm to 1.18 mm.

Physico-chemical characterization of the coco peat, shown in Table 1, was carried out in order to determine the properties that may affect or contribute to the effectiveness of the material in removing heavy metals from wastewater (Ong, 2010). Quantification of these properties is essential in confirming the potential of coco peat as a remediation material.

Based from the data obtained from the physico-chemical characterization, coco peat exhibited physico-chemical properties that may contribute or affect its capacity in removing heavy metal ions from aqueous solution. These properties support the material's potential as a good alternative to current heavy metal removal technologies.

Table 1. Coco Peat Physico-Chemical Properties Characterization Results

Parameter	Ong, 2009	Literature
Moisture Content, % w/w	17.47	
pH	5.70	5.0 – 6.8[b]
Bulk Density, g/cm^3	0.075	
Coefficient of Uniformity	3.00	
Coefficient of Gradation	0.96	
Effective Particle Size, mm	0.23	
Total Organic Matter, % w/w dry basis	96.93	94 – 98[b]
Lignin, % w/w dry basis	59.02	35.1[c]; 43.08[d]
Cellulose, % w/w dry basis	28.30	36.6[c]; 32.43[d]
Hemicellulose, % w/w dry basis	8.72	8.38[d]
Extractives (Alcohol-Benzene), % w/w dry basis	2.24	4.9 (Hot Water)[c]
Cation Exchange Capacity, meq/100g	151	60 – 130[c]
Anion Exchange Capacity, meq/100g	0.068	
Specific Surface Area, m^2/g	0.1159	7.42[e]
Trace metal concentration, mg/kg		
copper	3.9	3.12[c]
iron	441	121[c]
lead	ND[a]	0.175[c]

[a]ND means none detected at the method detection limit of 0.50mg/kg for Pb;
[b]Golden Harvest Organics LLC, 2008;
[c]Conrad and Hansen, 2007;
[d]Abad et al., 2002;
[e]Suksabye et al., 2007

Batch Experiments

Several batch experiments (Parcon (2010), Pingul (2010), Waskita (2010), Sta. Rosa and Torres (2010) were conducted to determine equilibrium and kinetic behaviour of lead, copper, cadmium and zinc sorption on coco-peat. The competitive sorption of the different heavy metal ions on coco-peat was also investigated (Erejer and Romero, 2009). Effect of particle size on the sorption behaviour was also determined (Pingul, 2009). The findings can be summarized as follow:

a) The adsorption kinetics of lead and copper on coco peat can be described by a pseudo-second order kinetic model, which suggests that the rate-limiting step is chemical biosorption.
b) An increase in pH from 2.5 to 4 also increased the amount of lead and copper sorbed, for both single and binary systems. There is also a large increase in the initial sorption rate with an increase in pH.
c) The adsorption capacities of both lead and copper decreased in the binary systems compared to single-solute systems, which suggests competition between ions for active sites. Lead also showed greater affinity for coco peat than copper.

d) The initial sorption rates for both lead and copper were reduced in binary systems compared to single-solute systems.
e) Experimental data for cadmium were found to fit more closely with the pseudo-second-order kinetic model, which suggests that the limiting-step in the adsorption process is the *chemisorption* mechanism.
f) Coco peat exhibited a very rapid cadmium adsorption rate of almost 96% removal after only the first 2 minutes of contact. Equilibrium was achieved within 2 hours, with maximum cadmium removal of 99.35%.
g) Varying coco peat particle size has a corresponding effect in the sorbent's cadmium-sorbing capacity, i.e. the smaller particle diameter means greater specific surface area, resulting in more surface binding sites and thus, higher cadmium removal.

Column Tests

Although batch tests are good measures to quantify sorption, column tests are laboratory methods which can simulate more closely filter beds where the solution is made to percolate through the filter media. The transport of the contaminant through the filter bed can best be understood by using an advection-dispersion model. The dispersion coefficient parameter of the heavy metal in the coco-peat can be determined by using this advection-dispersion model.

A column set-up with coco-peat as media was conducted by Ong (2010). The effect of the filtration rate on the efficiency of the removal of heavy metals was investigated by Aquino and Fontanilla (2009) using the column tests .Another set of experiments comparing the sorption capacity of coco-peat with sand, and with the mixed media (of sand and coco-peat) were also done by Budao and Calapre (2010). Based from these experiments, the following were observed:

a. Varying the flow rate of the column runs showed an effect on the sorption mechanism of lead ions on coco peat, e.g. the lower the flowrate is, the more ions are sorbed.
b. Heavy metal removal from single species and composite species aqueous solution follow the same selectivity sequence: Pb^{2+}>Cu^{2+}>Fe^{3+}, as shown in the heavy metal breakthrough curves and confirmed by the partition coefficient values obtained. The heavy metal selectivity sequence in the leaching tests was attributed mainly to influence of ionic size.
c. The configuration containing pure coco peat yielded the longest lag in the transport of heavy metals in column. Furthermore, the addition of sand did not contribute to the over-all sorption efficiency of coco peat.
d. The efficacy of the different porous media in sorbing heavy metals is thus ranked as follows: Coco peat >Mixed >Sand

Coco-Peat Activated Carbon

In this study of Keoduangchai (2011) , the fresh coco peat was washed several times with distilled water, then dried in oven for 24 h at the temperature of 105 ºC. The precursor was impregnated with $ZnCl_2$ at the impregnation ratio of 3:1 ($ZnCl_2$: Coco peat). The mixed material was then dried in oven for 12 h at the temperature of 105 ºC. The activation process was conducted in the following steps: (1) The impregnated sample was carbonized in the furnace at 250ºC for 100 min of the approximate heating rate 10-12 ºC/min; (2) The temperature of activation was increased up to 800 ºC under N_2 flow of 80 cm^3/min and maintained for 2 h then cooled to room temperature; (3) The product was washed with 0.1 mol/L HCl to remove residual chemicals then filtered and washed with distilled water until neutral pH; (4) The product was then dried in oven for 24 h before doing characterization.

Batch tests were conducted using various parameters such as contact time, initial metal concentrations, pH solution, adsorbent dosage, and temperature. The effects of equilibrium time (10-1440 min), pH (3-9), initial concentration of metal ions (10-50 mg/L), and adsorbent dosage (0.05-2.5 g) were examined and the optimum values obtained.

Based from the experiments conducted on coco peat activated carbon, the following conclusions can be made:

a. The prepared coco peat activated carbon, from chemical activation process, has high surface area than raw coco-peat.
b. The functional groups of prepared activated carbon were altered by carbonizing and activating temperature.
c. In the adsorption process, the metal adsorption kinetics fitted well with the pseudo second-order kinetic model on all metals tested.

Pilot Scale Reactor

Studies were also undertaken to accomplish the objectives related to the design, construction, and simulation of the Coco Peat Filter Bed Reactor (Espiritu, 2011). The set-up is an open-top box type structure with dimension of 1.2 m on all sides, and using transparent acrylic board 13-mm thick as walls. Gravity flow was applied for the system with a 1% gradient applied at the bottom of the filter bed. The filter medium is fixed-bed composed of sandy soil, gravel, coarse sand and coco peat. Figure 1 shows the Vertical Flow Filter Bed Design.

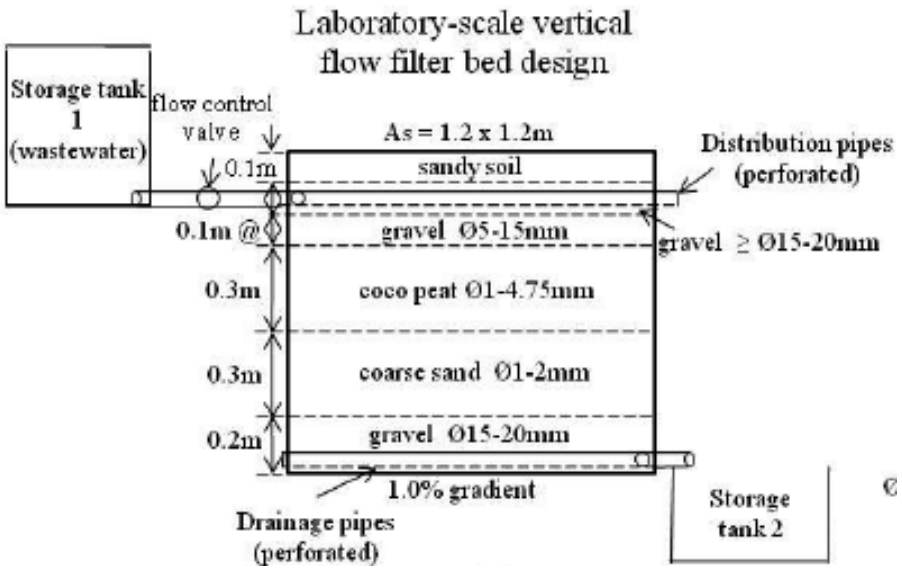

Figure 1. Filter bed design (Espiritu, 2011)

Based from the experiments conducted using the filter bed, the following were observed:

a) The filter bed reactor with coco peat as sorbent material was able to establish a copper removal of 97.64% or better for the five-month period.
b) Based on the concentration-depth profile and using the Hydrus modeling software, the reactor can be used up to 10 years before it gets fully saturated with copper ions.

On-Going and Future Activities

A reactor has been installed in the field (in Camarines Norte) in September 2012, and monitoring of its effectivity is being conducted. This is the first time that a reactor will be treating the actual wastewater. All previous laboratory experiments made use of synthetic wastewater.

In the laboratory, settling tests are being conducted using the actual wastewater. The settling characteristics will be determined to recommend improvements on the design of the settling tank.

According to the producers of the coco-coir, its estimated useful life is 5 years. Thus, this is another issue that the research wishes to address. There is an on-going study to investigate the changes that the coco-peat is undergoing to shed light on its useful life.

Research Utilization

To be able to have our research utilized by the small-scale miners, a close partnership needs to be established. For this project, a linkage has been formed with the *barangay* (village) officials to seek their support for the project. This is an important component for the project to succeed.

Conclusions

This paper discussed the research project entitled "Development and Testing of Coco-peat Filter Bed as Sorbent Material". The studies completed, done mostly on the laboratory-scale, show that coco-peat is a viable material for sorption, due to its sorption capabilities, as well as its being locally-availabe, abundant and cheap. The current studies are being done in the field, testing actual mine wastewater. For the research to be utilized by the industry, a partnership with the small-scale miners has been forged.

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References

[1] Annual Technical Report, Year 3, *Development and Testing of Coco-Peat as Filter Bed Material.* Report of Project B, 2012.

[2] M. Abad, P. Noguera, R. Puchades, A. Maquieira, and V. Noguera, "Physico-chemical and chemical properties of some coconut coir dusts for use as peat substitute for containerized ornamental plants", *Bioresources Technology, Vol.*82, pp. 241-245, 2002.

[3] Harold Aquino, and Leah Fontanilla. *Effect of flow rates on the removal of lead ions from aqueous solution using coco peat as sorbent material.* Thesis (BS). University of the Philippines Diliman, Philippines, 2009.

[4] C.M. Budao, and J.L. Calapre. *Designing a filter medium for treating mining waste water using mixtures of coco peat and mayon sand*. Thesis (BS). University of the Philippines Diliman, Philippines, 2011

[5] *"Coco Peat! It can't be beat!*." Golden Harvest Organics LLC, Available: www.ghorganics.com/Cocopeat.html.
[6] K. Conrad, and H.C.B. Hansen, "Sorption of zinc and lead on coir", Bioresource Technology, Vol. 98, pp. 89-97, 2007.
[7] Shiela I, Erejer, and Jomar Paul B. Romero. *Competitive sorption of copper and zinc in aqueous solution on coco peat using batch experiment*. Thesis (BS). University of the Philippines Diliman, Philippines, 2011.
[8] Danilyn Espiritu. *Evaluation of a laboratory-scale vertical flow filter bed using coco peat as a sorbent material to remove copper in aqueous solution*. Thesis (MS). University of the Philippines Diliman, Philippines, 2011.
[9] D. Espiritu, and E.L. Sicangco. *Determination of the sorptive capacity of coco fiber and coco peat in the sorption of zinc*. Department of Civil Engineering, University of the Philippines Diliman. Thesis (BS). University of the Philippines Diliman, Philippines, 2007.
[10] Keoduanchai Keokhampui. *Removal of heavy metals from mine wastewater using activated coco peat.* Thesis (PhD). University of the Philippines Diliman, Philippines, 2011.
[11] Kukuh Jalu Waskita. *Removal of copper, lead and zinc in aqueous solution using coco-peat: A study on competitive sorption using batch experiments*. Thesis (MS). University of the Philippines Diliman, Philippines, 2012.
[12] D.C. Ong. *Removal of heavy metals from single species and composite species aqueous solutions using coco peat as sorbent material*. Thesis (MS), College of Engineering, University of the Philippines, Diliman, Quezon City, Philippines, 2010.
[13] M.R. Parcon, "Kinetics of adsorption of lead and copper on coco peat", *Engineering Research and Development for Technology Proceedings 5th ERDT Conference Philippine Competitiveness Through ERDT*, Manila, Philippines, 2010.
[14] S.M. Pingul, "Evaluation of the efficiency of coco peat in adsorbing cadmium (II) using batch test", *Engineering Research and Development for Technology Proceedings 5th ERDT Conference Philippine Competitiveness Through ERDT*. Manila, Philippines, 2010.
[15] P. Suksabye, P. Thiravetyan, W. Nakbanpote, and S. Chayabutra, "Chromium removal from electroplating wastewater by coir pith", *Journal of Hazardous Materials, Vol.* 141, pp. 637–644, 2010.
[16] P. Suksabye, P. Thiravetyan, and W. Nakbanpote, "Column study of chromium (VI) adsorption from electroplating industry by coconut coir pith", *Journal of Hazardous Materials,* Elsevier, Vol. 160, pp.56-62, 2008.
[17] D.D. Sta. Rosa, and R.O. Torres. *Determination of distribution coefficient for lead and copper sorption on coco peat.* Thesis (BS). University of the Philippines Diliman, Philippines, 2010.