Sorption of Heavy Metal Ions from Mine Wastewater by Activated Carbons Prepared from Coconut Husk*

[1]W. K. Buah and [1]J. R. Dankwah
[1]University of Mines and Technology, P.O. Box 237, Tarkwa, Ghana

Buah, W. K. and Dankwah, J. R. (2016), "Sorption of Heavy Metals from Mine Wastewater by Activated Carbons Prepared from Coconut Husk", *Ghana Mining Journal,* Vol. 16, No. 2, pp. 36 - 41.

Abstract

A study on sorption of heavy metal ions: Lead (Pb^{2+}), Copper (Cu^{2+}) and Cadmium (Cd^{2+}) from mine wastewater by activated carbons prepared from coconut husk was conducted. The activated carbons were prepared by carbonisation of the husk at 900 ºC pyrolysis temperature, followed by steam activation of the pyrolysis derived char. Activation was also performed at 900 ºC for various durations at steam addition rate of 0.2 mol/h/g in a Gas Fired Static Bed Pyrolysis-Activation Reactor. The derived activated carbons were contacted with mine wastewater containing heavy metal ions to assess their heavy metal ions adsorption potential. The results show that the activated carbons efficiently adsorbed the heavy metal ions from solution, reducing concentrations of Pb^{2+}, Cu^{2+} and Cd^{2+} from 1.56 mg/L, 1.87 mg/L and 0.69 mg/L respectively to below Ghana Environmental Protection Agency (GEPA) standards of 0.10 mg/L, 1.30 mg/L and 0.03 mg/L for Pb^{2+}, Cu^{2+} and Cd^{2+} respectively. The significances of this study are that, the conversion of the coconut husk to activated carbons provides a solution to environmental problems associated with dumping of the waste and also provides valuable products capable of reducing the effects of heavy metals in wastewater.

Keywords: Coconut Husk, Activated Carbon, Heavy Metal, Adsorption

1 Introduction

Various operations such as mineral processing tailings disposal, illegal mining, domestic waste disposal and many others result in the release of heavy metals into water bodies. The presence of these metals including Cadmium (Cd), Arsenic (As), Chromium (Cr), Thallium (Tl), and Lead (Pb), having relatively high densities and are toxic or poisonous at low concentrations in water bodies, is a major environmental concern (Duruibe *et al.*, 2007; Koedrith *et al*., 2013; Momodu and Anyankora, 2010).

Some of these metals are good and essential for humans in little quantities. They, however, have the ability to bio accumulate. There is therefore the tendency for compounds of heavy metals to accumulate in living things any time they are taken up and stored faster than they are broken down resulting in sickness (Duruibe *et al.*, 2007; Koedrith *et al*., 2013).

For example, cadmium represents a health risk via accumulation in living tissue and has been associated with an increased risk of lung cancer, emphysema, kidney damage and in extreme circumstances, damage to bones and joints (Gimba *et al*., 2015; Probert *et al*., 1987; Järup and Agneta, 2009). Mercury and mercury compounds give rise to toxic effects associated with the central nervous system, the major areas affected being associated with the sensory, and auditory functions as well as those concerned with co-ordination (William, 2005). Lead exposure has been associated with disfunction in the haematological system and central nervous system. Decreases in intelligence and behaviour have been reported in children subject to exposure of increased levels of lead (Mason, *et al*., 2014; Hou, 2013; Williams, 2005).

One of the ways used to remove the metal ions from wastewater is by adsorption from the water using activated carbon (Bernard *et al*., 2013). The activated carbon used in Ghana is mostly imported from other countries at a high cost. There are, however, local materials such as coconut husk, coconut shell and corn cobs in large quantities (Buah *et al*., 2014) that can be considered for activated carbon production and used for adsorption of heavy metal ions from water.

Coconut palms (*Cocos nucifera*) are grown abundantly in Ghana, primarily, for the oil-rich copra contained inside the coconuts (Fig. 1). In a mature coconut, typical of what was used in this study, the white meat – copra (28 wt%) is surrounded by a hard protective shell (12 wt%) and a thick husk (35 wt%). This husk surrounding the large seed is made up of 30 wt% fibre and 70 wt% pith material (van Dam, 2004; Thampan, 1991). On a very minor scale, the coarse coir fibres are traditionally extracted from the husk for the production of mats, brushes and padding of mattresses, while the copra is extracted for oil production. A greater percentage of the hard shell and fibre end up in landfills as waste and may support bushfires, which are undesirable.

*Manuscript received March 16, 2016
Revised version accepted September 16, 2016
http://dx.doi.org/10.4314/gm.v16i2.5

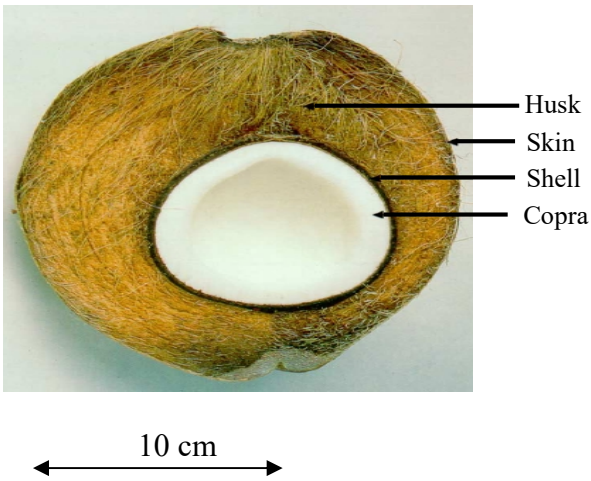

Fig. 1 Cross Section of a Coconut showing the Husk

This paper investigated production of activated carbons from coconut husk and assessed the derived activated carbons for heavy metal ions adsorption. The activated carbons were produced by carbonisation of the husks in a Gas Fired Static Bed Pyrolysis-Activation Reactor system followed by activation of the carbonised coconut husk for various durations. The derived activated carbons were characterised and then contacted with wastewater samples containing copper, cadmium and lead to determine their heavy metal ions adsorption performance.

2 Resources and Methods Used

2.1 Materials Preparation

The coconut husk was obtained from the waste stream of a coconut oil processing plant in Takoradi in Western Region of Ghana. The husk as received of particle size range of 40 – 100 mm were washed with water and dried at 110 °C in an oven till constant weight was achieved before carbonisation. A sample of the dried husk was pulverised to -1 mm and used to determine the proximate and ultimate analyses of the sample using thermogravimetric analysis (TGA) in a Shimadzu TGA-50H. The sample contained 4.21 wt% moisture, 4.40 wt%, ash, 64.95 wt% volatile matter and 26.50 wt% fixed carbon. The carbon, hydrogen and nitrogen contents of the husk were also determined using a FlashEA 1112 analyser as 50.57 wt%, 5.86 wt% and 0.30 wt% respectively.

De-ionised water obtained from the Mineral Engineering Laboratory of the University of Mines and Technology was used as the activation agent.
Waste water sample for the test work was collected from a tailings dam in a mining community in Tarkwa in the Western Region of Ghana. The sample was collected in a sample bottle and immediately placed in an 'ice chest' in ice packs and transported to the laboratory where analyses of heavy metal ions content were carried out within six hours using Atomic Adsorption Spectrophotometer. The analysis detected the concentration of Pb^{2+}, Cu^{2+} and Cd^{2+} as 1.56 mg/L, 1.87 mg/L and 0.69 mg/L respectively. The pH of the wastewater was 6.

2.2 Preparation of Activated Carbons from the Husk

The dried husk was carbonised in a gas fired static bed pyrolysis-activation reactor, designed and fabricated in Ghana (Buah *et al.*, 2014), at 900 ºC pyrolysis temperature to obtain char. This reactor has a stainless steel chamber of a rectangular cross-section, having a square groove positioned symmetrically at the bottom part of the reactor, which allows efficient heat transfer into the bed of material being pyrolysed. The design allows easy feeding of precursors as well as easy discharging of carbonised products. The char was kept in the final pyrolysis temperature for 60 minutes. This was allowed to ensure pyrolysis is carried to completion as much as possible. The weight of the char was taken after it had been allowed to cool. The char was then subjected to physical activation at 900 ºC activation temperature using steam as the activation agent. The steam activation was done at a water flow rate of 0.2 mol/h/g for 1.0 h, 1.5 h, 2.0 h and 2.5 h. The carbonisation and activation procedures were repeated.

The carbonisation and activation temperature of 900 ºC was chosen because other researchers (Guo and Lua, 2000; Bouchelta *et al*., 2008) used similar process conditions successfully for development of high quality activated carbons. For example, Guo and Lua (2000) successfully produced quality activated carbons at 900 ºC. In their investigations the effect of heating temperature on the properties of chars and activated carbons prepared from oil palm stones was studied. They established that as the activation temperature increased from 750 ºC up to 900 ºC, the Brunauer Emmett and Teller (BET) and micropore surface areas increased progressively since the activation process not only enlarged the pores created during the pyrolysis but also generated some new pores. However, at 950 ºC, the surface area, especially the micropore surface area dropped dramatically due to over-reaction of carbon with the activating agent.

2.3 Characterisation of the Derived Activated Carbon

2.3.1 Yield of activated carbons

The yield of activated carbon, resulting after activation of a given quantity of the carbonised

husk is calculated according to equation 1 as follows:

$$Yield,\quad Y = \frac{W_2}{W_1} \times 100\% \qquad (1)$$

where: W_1 = Initial dry mass of char (g) and W_2 = Dry mass of carbon after activation (g).

2.3.2 Determination of surface areas and pore volumes of the activated carbons

The surface areas of the derived activated carbons were determined by the Brunauer, Emmett, and Teller (BET) method (Gregg and Sing, 1982). In this determination adsorption of nitrogen by the activated carbon at 77K using a Micromeritics TriStar 3000 apparatus was carried out. The BET surface areas assessment was done by applying relative pressures ranging from 0.05 to 0.20. The total pore volumes of the derived activated carbons were estimated to be the liquid volumes of N_2 at a high relative pressure of 0.96, assuming the molecular cross-sectional area of nitrogen to be 0.162 nm^2. The micropore volumes were calculated by application of the Dubinin Radushkevich (DR) equation to the nitrogen adsorption isotherms of the activated carbons (Dubinin and Radushkevitch, 1947).

2.3.3 Heavy metal ions adsorption studies of the activated carbons

Batch adsorption experiment for each of the derived activated carbons was done by contacting 500 mL of the wastewater with 25 g of each of the activated carbons in a bevelled glass bottle. The bottles were placed on a roller and rotated at 150 rpm at a room temperature of 32 ^{o}C for a period of 120 min to ensure good mixing and carbon-wastewater contact. Solution samples were taken from the bottles every 15 minutes and filtered using Whatman filter paper. A Varian Fast Sequential Atomic Adsorption Spectrophotometer (Varian AA240FS) was used to analyse the concentrations of the different metal ions present in the filtrate. Repeat tests assessing the adsorption performance of the activated carbons were carried out.

3 Results and Discussion

3.1 Production of Activated Carbon

The yield of char obtained after carbonisation of a sample of the coconut husk was 27.05 wt%. Samples of the carbonised husk, subjected to steam activation for various durations, produced activated carbons. The yields of the derived activated carbons were dependent on the duration of activation as shown in Fig. 2 and were repeatable with relative standard deviation of not more than 1.04%. The decrease in yield is an indication of increasing carbon burn-off of the activated carbons as the activation time increased.

The carbon burn-off, resulting after activation of a given quantity of the carbonised husk can be calculated according to equation 2 as follows:

$$Burn-off,\quad BO = \frac{m_1 - m_2}{m_1} \times 100\% \qquad (2)$$

where: m_1 = Initial dry mass of char (g) and m_2 = Dry mass of carbon after activation (g).

It can therefore be deduced that the carbonised coconut husk exhibited a linear correlation between activation time and burn-off. Daud and Ali (2004) also observed, in a comparative study on the pore development of activated carbons produced from palm nut shell and coconut shell char, that both materials exhibited a linear correlation between activation time and burn-off.

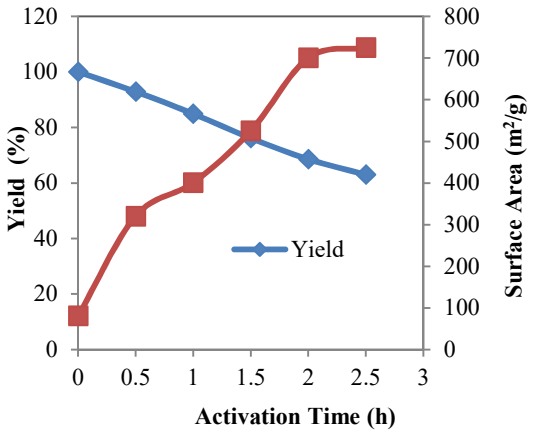

Fig 2 Yield of Activated Carbons Relative to Activation Time

3.2 Surface Area and Pore Volumes of the Activated Carbons

The BET surface area of the char obtained after pyrolysis of the husk at 900 ^{o}C without activation was 80.55 m^2/g. The surface area of the derived activated carbons increased with increasing activation hold time, reaching a value of 725.57 m^2/g after 2.5 hours of activation. The increasing activation time accompanied by increasing degree of carbon burn-off, corresponding to decreasing yield, as deduced from Fig. 2 resulted in development of rudimentary pores and increase in the surface area of the activated carbons.

From the results of total pore volumes, obtained from N_2 adsorption isotherms of the derived activated carbons, determination of the micropore volumes from the DR plots of the isotherms, the mesopore volumes were calculated and the results are shown in Fig. 3.

The results shows that the total and micropore volumes of the activated carbons, produced after various activation hold times at 900 °C, increased with increase in the activation hold time. There was repeatability in the surface areas and pore volumes of the derived activated carbons with a relative standard deviation of not more that 0.55%.

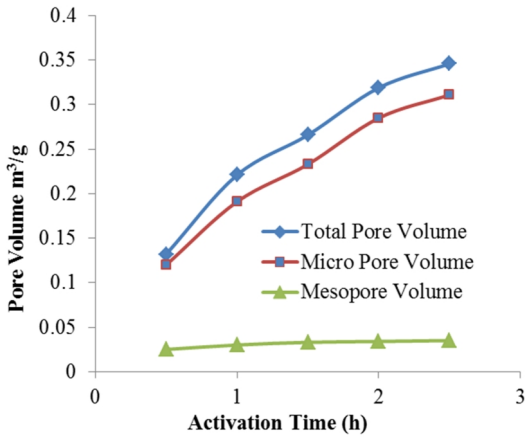

Fig. 3 Pore Volumes of the Activated Carbons Relative to Activation Time

3.3 Heavy Metal Ions Adsorption by the Activated Carbons

The results of adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} from the wastewater by the various coconut husk activated carbons are presented in Figs. 4 to 6.

3.3.1 Adsorption of Copper

From Fig. 4a, the copper concentration of 1.87 mg/l of the wastewater before adsorption reduced to a level below the GEPA threshhold of 1.30 mg/l after contacting with the activated carbons and even the unactivated coconut husk char. The unactivated char recorded the lowest adsorption performance, and this is expected due to its low surface area as seen in Fig. 2 and low pore volume as can be deduced from Fig 3. The adsorption performance of the derived carbons was found to increase with increasing activation time. All the activated carbons adsorbed at a faster rate in the first 15 mins of adsorption. Then after, the rate of adsorption slowed down but adsorption was complete at 45 min for the activated carbon produced after 150 min of activation as shown in Fig. 4b, which is an amplified version of Fig. 4a.

3.3.2 Adsorption of Cadmium

All the activated carbons had relatively high rate of adsorption during the first 15 min of adsorption as seen in Fig. 5a.

From Fig 5b, an amplified graph of Fig. 5a for legibility of trend of adsorption of cadmium in relation to contact time, it can be observed that the coconut husk chars activated at 30 min, 60 min and the unactivated char could not reduce cadmium concentration to below the GEPA standard of 0.03 ppm. The 90 min, 120 min and 150 min activated carbons reduced cadmium concentration to below the GEPA standard. Adsorption by the activated carbons was activation time dependent. The longer the carbons were activated the more their cadmium adsorption capacities.

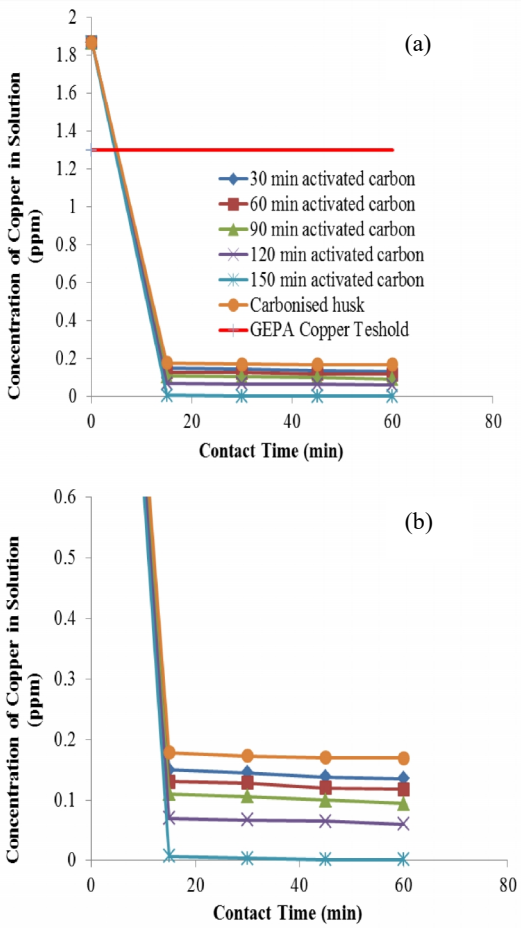

Fig. 4 Concentration Profile of Copper in the Wastewater in Relation to Adsorption Time: (a) For 0 to 1.87 ppm of Copper Concentration (b) For 0 to 0.60 ppm of Copper Concentration

3.3.3 Adsorption of Lead

From Fig 6, it can also be observed that there was fast adsorption rate of lead by the activated carbons during the first 15 min of adsorption. Adsorption was highest after 30 min. Above 30 min adsorption decreased and this could be due to release of the metal ion back into the solution and later reabsorbed at time 60 min. The unactivated coconut husk had a comparable adsorption performance to that of the activated carbons.

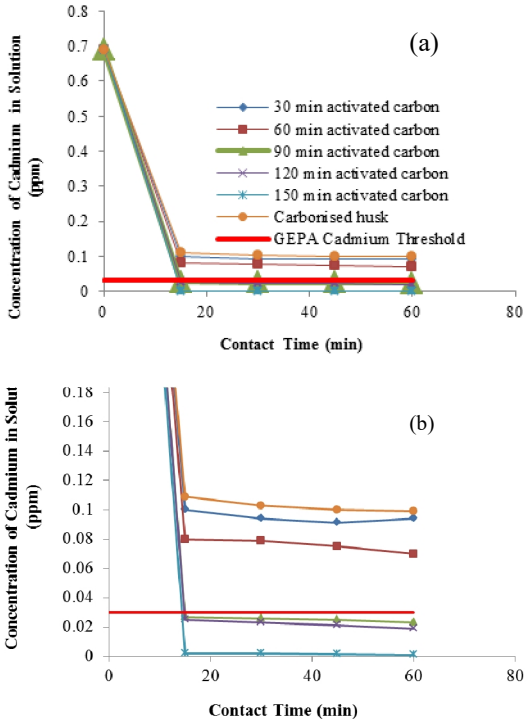

Fig. 5 Concentration Profile of Cadmium in the Wastewater in Relation to Adsorption Time: (a) For 0 to 0.69 ppm of Cadmium Concentration (b) For 0 to 0.18 ppm of Cadmium Concentration

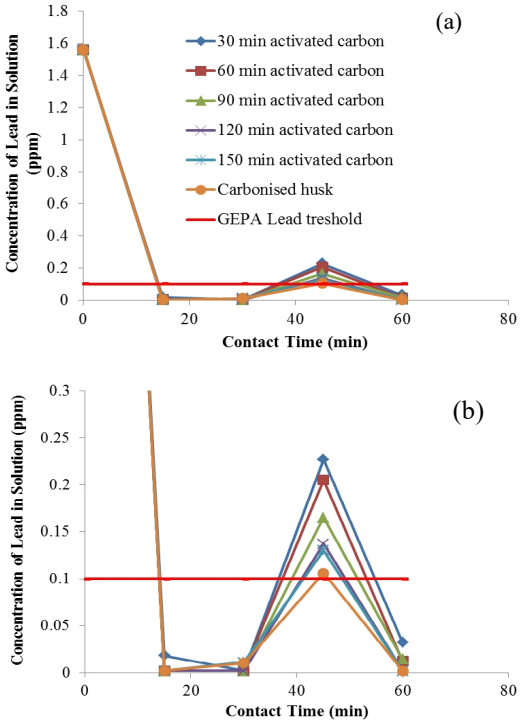

Fig. 6 Concentration Profile of Lead in the Wastewater in Relation to Adsorption Time: For 0 to 1.56 ppm of Lead Concentration (b) For 0 to 0.30 ppm of Lead Concentration

4 Conclusions

Coconut husk based ctivated carbons of varrying surface areas and pore volumes were successffully prepared. The derived activated carbons were used for the adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} from waste water, reducing their concentration from 1.56 mg/L, 1.87 mg/L and 0.69 mg/L respectively to below Ghana Environmental Protection Agency standards. This paper demonstrates the conversion of waste coconut husk to activated carbons and their application in heavy metal ions adsorption from waste water. The significance of this study is twofold. Firstly, the conversion of the coconut husk waste to activated carbons provides a solution to environmental problems associated with dumping of the waste and secondly provides valuable products capable of reducing the effects of heavy metals in wastewater.

Acknowledgements

The Authors are very grateful to Mr Landry and Miss Rosalyn Yeboah, both products of the University of Mines and Technology, for their assistance during the laboratory investigations.

References

Bernard, E., Jimoh, A., Odigure, J. O. (2013), "Heavy Metals Removal from Industrial Wastewater by Activated Carbon Prepared from Coconut Shell", *Research Journal of Chemical Sciences*, Vol. 3, pp. 3 - 9.

Bouchelta, C., Medjram, M. S., Bertrand, O. and Bellat, J. P. (2008), "Preparation and characterization of activated carbon from date stones by physical activation with steam", *J. Anal. Appl. Pyrolysis*, 82, pp. 70 - 77.

Buah, W. K., Kuma, J. S. Y. and Williams, P. T (2014), "Activated Carbon Prepared in a Novel Gas Fired Static Bed Pyrolysis-Gasification/Activation Reactor for Gold Di-Cyanide Adsorption", *3rd UMaT Biennial International Mining and Mineral Conference,* pp. 243-250.

Daud, W. M. A. W. and Ali, W. S. W. (2004), "Comparison on pore development of activated carbon produced from palm shell and coconut shell", *Bioresource Technology*, 93, pp. 63 – 69.

Dubinin, M. M. and Radushkevitch (1947), *Proc. Acad. Sci. USSR,* 55, p.331.

Duruibe, J. O., Ogwuegbu, M. O. C. and Egwurugwu, J. N. (2007), "Heavy metal pollution and human biotoxic effects", *International Journal of Physical Sciences*, Vol. 2 (5), pp. 112-118.

Gimba, C. E., Ndukwe, G. I., Paul, E. D., Habila, J. D., Madaki, L. A. (2015), "Heavy Metals (Cd, Cu, Fe, Mn and Zn) Assessment of Groundwater in Kaltungo LGA, Gombe State,

Nigeria". *International Journal of Science and Technology*, 4, pp 44 - 49.

Gregg, S. J. and Sing, K. S. W. (1982), In: *Adsorption, Surface Area and Porosity*, Academic Press, London, 303 pp.

Guo, J. and Lua. A. C. (2000), "Effect of Heating Temperature on the Properties of Chars and Activated Carbons Prepared from Oil Palm Stones", *Journal of Thermal Analysis and Calorimetry*, 60, pp. 417 - 425.

Hou, S., Yuan, L., Jin, P., Ding, B., Qin, N., Li, L., Liu, X., Wu, Z., Zhao, G. and Deng, Y. (2013), "A clinical study of the effects of lead poisoning on the intelligence and neurobehavioral abilities of children", *Theoretical Biology & Medical Modelling*, 10, pp. 10 - 13.

Järup, L. and Agneta, A. (2009), "Current status of cadmium as an environmental health problem", *Toxicology and Applied Pharmacology,* Vol. 238, Issue 3, pp. 201–208.

Koedrith, P., Kim, H., Weon, J. and Seo, Y. R. (2013), "Toxicogenomic approaches for understanding molecular mechanisms of heavy metal mutagenicity and carcinogenicity", *International Journal of Hygiene and Environmental Health*, Volume 216, Issue 5, Pages 587-598.

Mason, L. H., Harp, J. P. and Han, D. Y. (2014), "Pb Neurotoxicity: Neuropsychological Effects of Lead Toxicity", *BioMed Research International*, Volume 2014, Article ID 840547, 8 pp.

Momodu, M. A. and Anyankora, C. A. (2010), "Heavy Metal Contamination of Ground Water". *Journal of Environmental and Earth Science*, 2, pp. 39 - 43.

Probert, S. D., Kerr, K. and Brown, J. (1987), Harnessing energy from domestic, municipal and industrial refuse, *Applied Energy*, 27, pp. 89 - 168.

Thampan, *P. K. (1991), Handbook on Coconut Palm*, Oxford and IBH Publishing Co., New Delhi, 248 pp.

van Dam, J. E. G., van den Oever, M. J. A., Teunissen, W., Keijsers, E. R. P. and Peralta, A. G. (2004), "Process for production of high density/high performance binderless boards from whole coconut husk Part 1: Lignin as intrinsic thermosetting binder resin", *Industrial Crops and Products,* 19, pp. 207 - 216.

Williams, P. T. (2005), *Waste Treatment and Disposal*, 2nd Edition. John Wiley & Sons Ltd, Chichester, UK, 380 pp.

Authors

W. K. Buah is currently an Associate Professor at the University of Mines and Technology, Tarkwa, Ghana. He holds a PhD in Waste Processing Engineering from the University of Leeds, Leeds, UK and a Master of Science Degree in Minerals Processing Engineering from the Mining Institute of Krivoy Rog, Krivoy Rog, Ukraine. He is a member of the Society for Mining, Metallurgical and Exploration Engineers (SME) and the Chattered Institute of Waste Management, UK. His current research interests include minerals processing and extractive metallurgy, waste management, pyrolysis-gasification of wastes and biomass to produce valuable products, including activated carbon for gold adsorption.

James R. Dankwah obtained his PhD from the School of Materials Science and Engineering, UNSW-Australia, MSc (Process Metallurgy) from the Norwegian University of Science and Technology and BSc (Metallurgical Engineering) from the Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. His current research areas include iron and steelmaking, high-temperature metallurgical processes, utilisation of waste polymers in metal extraction processes and recycling agricultural waste into building blocks materials for affordable housing for rural folks.