International Journal of Engineering & Technology, 7 (3.11) (2018) 241-244

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Sorption of lead from aqueous system using cocoa pod husk biochar: kinetic and isotherm studies

Soon Kong Yong[1,*], **Jesielyna Leyom**[1], **Chia Chay Tay**[1], **Suhaimi Abdul Talib**[2]

[1]Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[2] Faculty of Civil Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
**Corresponding author E-mail: yongsk@salam.uitm.edu.my*

Abstract

Cocoa pod husk (CPH) was pyrolyzed at 500°C to produce biochar (CPHB) for sorption of lead (Pb) from aqueous system. Chemical characterization for CPHB was conducted using Fourier transform infrared (FTIR) spectroscopy, Boehm titration and X-ray fluorescence (XRF) spectroscopy. Sorption parameters for CPHB (i.e., sorbent dosage, pH, contact time, and Pb concentration) were optimized. Elemental compositions for CPHB are C (66% w/w), O (19% w/w), and N (2% w/w). The ash of CPHB consists of calcium oxide (CaO) (4.6% w/w) and potassium oxide (K_2O) (4.2% w/w), with negligible amount of heavy metals (1% w/w). Upon treatment with artificial Pb wastewater, FTIR spectra for CPHB revealed shifting of ν_{asymm}(COO-) and ν_{symm}(COO-) bands from 1560 cm^{-1} to 1575 cm^{-1} and 1416 cm^{-1} to 1398 cm^{-1}, respectively. The optimum sorption parameters were determined (i.e., sorbent dosage: 1.0 g/L; pH 5; input Pb concentration; 50 mg/L; and sorption time: 210 minutes). Sorption of Pb by CPHB was best described by pseudo-second-order kinetic model (R^2= 0.835), and Langmuir isotherm model (R^2= 0.962). Maximum Langmuir Pb sorption capacity for CPHB (q_{max}) was 69.9 mg/g. These findings suggested that the sorption of Pb by CPHB may have occurred through (1) coordination with polar groups (i.e., carboxylate and phenolate) and (2) precipitation with alkaline materials (i.e., CaO and K_2O).

Keywords: *Carbon; complexation; heavy metals; pyrolysis; solid waste management.*

1. Introduction

Groundwater in Malaysia is contaminated with toxic lead (Pb) [1]. Exposure of Pb in groundwater may cause damage to kidney, nervous system and reproductive systems. Conventional treatment that consists of physical and chemical processes may be effective in reducing Pb concentration groundwater or leachate. However, large scale consumption of energy and chemicals increase the cost of treatment [2]. Biosorption may offer a cheaper solution for effective removal of trace Pb from groundwater. Cheap and abundant biomass from the agricultural sector can be utilized as biosorbent for decontamination of Pb in groundwater.

Malaysia produces large amount of agricultural biomass from cocoa plantation. The cocoa pod husk (CPH) that accounts for 70 - 75% of the total weight of the whole cocoa fruit [3], has no commercial value and is usually disposed in landfill. Recently, CPH has shown potential in decontaminating heavy metals (i.e., zinc) in contaminated wastewater [4]. The sorption capacity of CPH for heavy metals can be enhanced further when pyrolyzed at anoxic condition, where the dehydration of sap cells in CPH will produce a carbon-rich and porous material called cocoa pod husk biochar (CPHB). In addition, biochar prepared at high temperature (i.e., >500°C) is more stable [5], and may be suited for decontamination of Pb from aqueous system.

To the best of our knowledge, Pb sorption kinetics and isotherms for CPHB have never been reported. This study aims to investigate the potentials of CPHB as sorbent for Pb, by measuring maximum Pb sorption capacity from artificial groundwater, and to determine the Pb sorption mechanism of CPHB.

2. Materials and methods

2.1. Synthesis of CPHB

Cocoa pod husk (CPH) was collected from the Malaysian Cocoa Board Centre of Research and Development, in Jengka, Pahang, Malaysia. The as-received CPH was rinsed with deionized water (DI) to remove impurities. Then, cleaned CPH was oven-dried at 60°C for 72 hours. The dried CPH was pulverized with a hammer-mill machine and sieved with a 70-mesh screen to 200 µm in particle diameter. The fine CPH particles was pyrolyzed in a furnace at 500°C under nitrogen gas ambient for 2 hours to produce CPHB. The CPHB was washed thoroughly with DI water, oven-dried at 60°C for 72 hours and homogenized for further analyses.

2.2. Characterization for CPHB

The chemical characterization of the cocoa pod husk was done by using FTIR, XRF and Boehm Titration. The functional groups present in the cocoa pod husk biochar were characterized by using the Fourier transform infrared (FTIR) spectroscopy. After the treatment with Pb(II), the dried biochar was again characterized with FTIR in order to identify any changes that occur after the treatment process. Another instrument that was used in this study is the XRF to identify the presence of pre-contained Pb^{2+} compound in the biochar sample

The pH for CPHB was determined from 10 mmol/L calcium chloride ($CaCl_2$) solution (CPHB/solution ratio 1:10) using a calibrated pH meter. The elemental analyses were conducted at the Institute of Science, UiTM Shah Alam, using elemental analyser (Thermofinnigan Flash EA2000, UK), and XRF spectroscopy (PANalytical Epsilon3-XL, Netherlands). The FTIR spectra was recorded using FTIR spectrometer (Perkin Elmer Spectrum One, USA) on KBr disc containing 5% w/w of samples. The average FTIR spectra for CPHB and Pb-treated CPHB were determined from 64 scans between 4000 cm^{-1} and 400 cm^{-1} wavenumbers. Boehm titration was conducted according method described by Goertzen *et al.* (2010) (Figure 1).

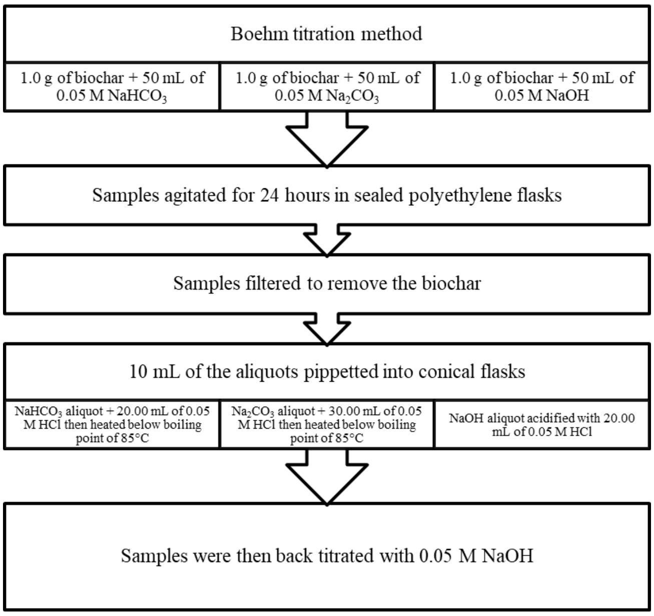


Fig. 1: Flowchart for Boehm titration

The amount of functional groups on the surface of CPHB were calculated equation (1) [6]:

(1)

where $[R_b]$ is the concentration of base reacted with CPHB (mmol/L); V_r is the volume of base reacted with CPHB (L); [X] is the concentration of excess hydrochloric acid added (mmol/L); V_x is the volume of excess hydrochloric acid added (L); [T] is the concentration of NaOH titrant (mmol/L); V_t is the volume of NaOH titrant (L) and m is mass of CPHB used in Boehm titration (g).

2.3. Batch sorption experiments

Sorption experiment was conducted using 50 mg/L Pb nitrate solution as synthetic wastewater. Potassium nitrate (10 mmol/L) was added to lead nitrate solution as background electrolyte for maintaining ionic strength of Pb nitrate solution. Sorption experiment was optimized at five sorbent dosage values (i.e., 0.05, 0.10, 0.50, 1.0, 5.0 g/L), and five solution pH values (i.e., 3, 4, 5, 6, 7). Sorption kinetic was conducted at optimized solution pH and sorbent dosage. Nineteen data points were collected between 0 and 210 minutes of contact time. For sorption isotherm experiment, CPHB was contacted with five initial Pb concentrations (i.e., 10, 20, 30, 40, and 50 mg/L) at optimized solution pH, sorbent dosage and contact time. The mixtures were filtered with filter paper to separate spent CPHB. The residual Pb concentrations of the filtrates were analyzed using flame atomic absorption spectroscopy (FAAS) (Perkin Elmer Analyst 400, USA). The sorption capacity (q_t) was calculated using equation (2):

$$q_t = \frac{(C_o - C_t)V}{m} \tag{2}$$

where C_o and C_t are the initial and equilibrium Pb concentration (mg/L), respectively; V is the volume of residual Pb (L); and m is the dry weight of CPHB (g). The sorption data were analyzed with kinetic models (i.e., pseudo-first-order and pseudo-second-order) and isotherm models (i.e., Langmuir and Freundlich) (Table 1) [7].

Table 1: Non-linear kinetic models (pseudo-first-order & pseudo-second-order) and isotherm models (Langmuir & Freundlich)

Kinetic/isotherm models	Non-linear equation
Pseudo-first-order	$q_t = q_e(1-\exp(-k_1 t))$
Pseudo-second-order	$q_t = \frac{C_e^{2} k_2 t}{1+C_e k_2 t}$
Langmuir	$q_t = \frac{q_{\max} K_L C_e}{1+K_L C_e}$
Freundlich	$q_t = K_F C_e^{1/n}$

where q_e (mg/g) is the amount of the metal ions adsorbed at equilibrium (mg/g); t (minutes) is the contact time for CPHB and Pb nitrate solution; k_1 (min^{-1}) and k_2 (g/mg min) are the rate constant for the pseudo-first-order and pseudo-second-order equation, respectively; q_{max} is the maximum Langmuir sorption capacity of CPHB (mg/g); K_L is the Langmuir constant (L/mg); K_F is the Freundlich constant (mg/g); and n is the empirical constant (L/mg). The sorption data were fitted with non-linear kinetic and isotherm models using Sigmaplot 11.0 software.

3. Results and discussion

3.1. Characterization for CPHB

Elemental compositions for CPHB are shown in Table 1 (i). Cocoa pod husk biochar primarily consists of C (65.7%w/w), with 10.1%w/w of ash content. Further XRF analysis shows that the ash in CPHB constitutes CaO (4.6%w/w) and K_2O (4.2%w/w), and with negligible contents of CuO (0.03%w/w), ZnO (0.19%w/w) and MnO (0.46%w/w). Both CaO and K_2O are alkaline materials and may have contributed to the high pH (9.1 ± 0.32) of the CPHB in $CaCl_2$ solution. Based on the results from Boehm titration (Table 1 (ii)), the contents for phenolic and carboxylic groups on the surface of the CPHB are 0.75 mmol/g and 1.5 mmol/g, respectively.

Table 1: (i) Elemental and ash composition [%w/w] and **(ii)** functional groups composition [mmol/g] in CPHB

(i)

Elements	Composition [%w/w]
C	65.7
H	2.7
N	2.2
O	19.3
Ash	10.1

(ii)

Functional groups	Composition [mmol/g]
Carboxylic	1.5
Lactonic	0
Phenolic	0.75
Surface acidity	2.25
Surface basicity	0.66

The wavenumber values for bands in the FTIR spectra for CPHB and the Pb-CPHB are shown in Table 2. The presence of phenolic and carboxyl groups in Boehm titration experiment corroborates with the FTIR result. The strong $\nu(COO^{-})$ vibration band in the FTIR spectra CPHB were observed at 1575–1690 cm^{-1}. Upon treatment with Pb nitrate solution, the ν_{asymm}(C-O) and ν_{symm}(C-O) vibration bands of the carboxylate group shifted from 1560 cm^{-1} to 1575 cm^{-1}, and 1380 cm^{-1} to 1420 cm^{-1}, respectively. The $\Delta\nu(COO^-)$ value [$\nu_{asymm}(COO^-)$ - $\nu_{symm}(COO^-)$] in the Pb-CPHB FTIR spectra is 177 cm^{-1}, indicating that Pb(II) ions are chemically bonded to the carboxylate group through monodentate coordination (Figure 2) [8]. A shoulder at 1243 cm^{-1} in Pb-CPHB spectra was assigned to stretching vibration for phenolate group [9]. Two stretching bands of aliphatic hydroxyl groups in CPHB (at 1053 cm^{-1} and 1043 cm^{-1}, respectively [10]) remained similar even after treatment with Pb nitrate solution. Therefore, coordination of Pb(II) ions did not occur with the hydroxyl groups in CPHB.

Table 2: FTIR bands wavenumbers [cm^{-1}] for CPHB and Pb-CPHB

FTIR bands	Wavenumbers [cm^{-1}]	
	CPHB	Pb-CPHB
$\nu_{asymm}(COO^-)$	1560m	1575vs
$\nu_{symm}(COO^-)$	1416m	1398vs
ν(CH-OH)	1053vs	1053vs
$\nu(CH_2\text{-}OH)$	1043vs	1045vs

Note: Peak intensity (with respect to the strongest peak in the spectrum): vs (very strong) 80–100%, s (strong) 60–80%, m (medium) 40–60%, w (weak) 20–40%, vw (very weak) 0–20%; Bond vibration mode: ν = stretching, sym = symmetric, asymm = asymmetric

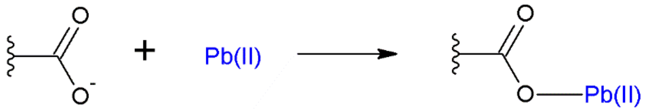
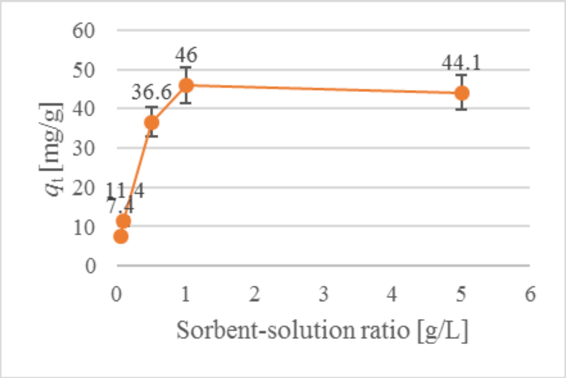


Fig. 2: Monodentate coordination of Pb(II) ion with the carboxylate group in CPHB

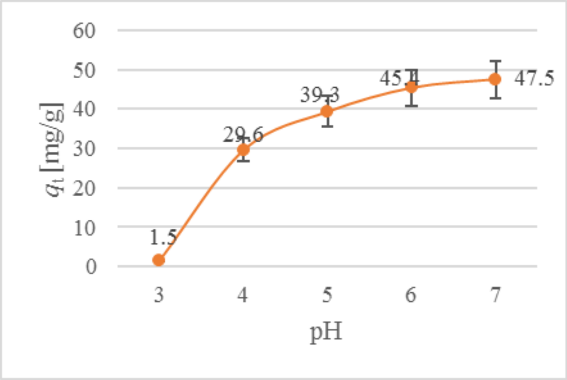
3.2. Batch sorption experiments

The q_t values [mg/g] as a function of initial solution pH and sorbent-solution ratio [g/L] are shown in Figure 3. The q_t values for CPHB increased with increasing in sorbent solution ratio and solution pH. The q_t values reached plateau when sorbent-solution dosage is 1.0 g/L, and solution pH is around 6-7. Sorption for Pb were enhanced possibly due to (1) stronger interaction between Pb(II) ions and deprotonated carboxyl group in CPHB, and (2) minor precipitation of Pb(II) ions to insoluble lead hydroxide, carbonate, phosphate or sulfate species [7].

The regression plots for non-linear kinetic and isotherm models are shown in Figure 4. Sorption data have high fitness to the pseudo-second-order kinetic model (R^2= 0.963) (Table 3), showing that the rate limiting step may be controlled by chemical process [11]. Sorption of Pb by CPHB is best described by the linearized Langmuir isotherm model (R^2= 0.962) (Table 4), indicating the Pb monolayer adsorbed on the homogenous surface of CPHB. The Langmuir constant (R_L) was 0.091-0.33, indicating that Pb sorption is a favourable process [11].

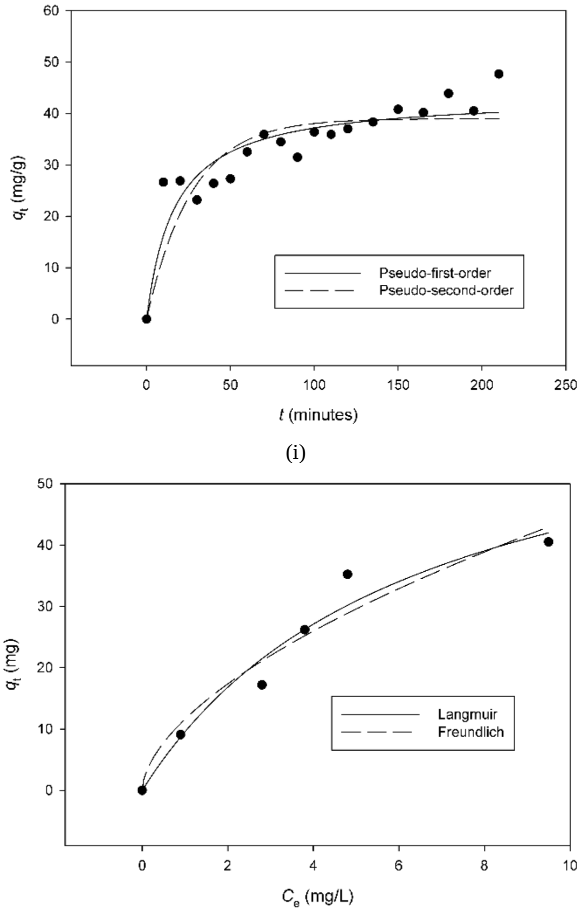


(i)



(ii)

Fig. 3: Lead sorption capacity for CPHB (q_t, mg/g) as a function of (i) sorbent/solution ratio (g/L), and (ii) solution pH



(i)

(ii)

Fig. 4: Non-linear regression plots for **(i)** kinetic models (pseudo-first-order & pseudo-second-order); and **(ii)** isotherm models (Langmuir & Freundlich)

Table 3: Kinetic models parameters for Pb sorption by CPHB

Kinetic models	Pseudo-first-order	Pseudo-second-order
R^2	0.753	0.835
q_e [mg/g]	39.0	43.5
k	0.0373	0.0014

Table 4: Isotherm models parameters for Pb sorption by CPHB

Isotherm models	Langmuir	Freundlich
R^2	0.962	0.946
q_{max} [mg/g]	69.9	-
K_L [mg/L]	0.158	-
K_f [mg/g]	-	11.6
n	-	1.720

Table 5 shows the $q_{\max}$ values for sorption of Pb(II) ions by various sorbents from recent literatures. The $q_{\max}$ value for CPHB (69.9 mg/g) is higher than most of the biomass except for *S. melongena* leaves. The $q_{\max}$ value for CPHB is also significantly higher than those of cocoa pod powder (5.31 mg/g) [12], and cocoa shell (6.54 mg/g) [13]. This demonstrates the benefits of pyrolysis on improving the sorption capacity of biomass. As a comparison with other pyrolyzed biomass sorbent available in Malaysia, the $q_{\max}$ value for CPHB is lower than palm shell activated carbon (95.2 mg/g) [14], but higher than bone powder (55.3 mg/g), active carbon (41 mg/g), and commercial carbon (27.3 mg/g) [15].

Table 5: Langmuir maximum sorption capacities (mg/g) of CPHB and selected biomass derived sorbents and from previous studies

Sorbent	$q_{\max}$ (mg/g)	Reference
PKS activated carbon	95.2	[14]
S. melongena leaves	71.4	[16]
CPHB	69.9	This study
Grape stalk waste	49.9	[17]
Sago waste	46.6	[18]
G. hirsutum biomass	45.0	[19]
L. erythropterus	16.7	[20]
Cocoa pod powder	5.3	[21]
Date pits	2.9	[22]
Mango stone	1.9	[21]

4. Conclusion

Pyrolysis of CPH has successfully produced CPHB with high Pb sorption capacity that is comparable to commercial sorbents available in Malaysia. Lead ions monolayer may have adsorbed on the surface of CPHB through monodentate coordination bonding with carboxylate or phenolate groups. The presence of alkaline metal oxides (i.e., CaO and K_2O) in the ash of CPHB may have caused precipitation of Pb(II) ions in the aqueous phase, and contributed to the high Pb sorption capacity for CPHB. Nevertheless, the practical use of CPHB for treating Pb in water may require further studies to understand its real potential.

Acknowledgement

The authors would like to thank the Ministry of Higher Education for financially supporting this research project through the Fundamental Research Grant Scheme (FRGS) [600-RMI/FRGS 5/3 (0128/2016)], the Universiti Teknologi MARA for providing research facility.

References

[1] S. Kathirvale, M.N.M. Yunus, K. Sopian & A.H. Samsuddin, Energy potential from municipal solid waste in Malaysia. Renewable energy 29 (2004) 559-567.

[2] L.A. Manaf, M.A.A. Samah & N.I.M. Zukki, Municipal solid waste management in Malaysia: Practices and challenges. Waste Management 29 (2009) 2902-2906.

[3] G. Cruz, M. Pirilä, M. Huuhtanen, et al., Production of activated carbon from cocoa (Theobroma cacao) pod husk. J Civil Environment Engg 2 (2012) 1-6.

[4] V.O. Njoku, Biosorption potential of cocoa pod husk for the removal of Zn(II) from aqueous phase. Journal of Environmental Chemical Engineering II (2014) 881-887.

[5] B.P. Singh, A.L. Cowie & R.J. Smernik, Biochar Carbon Stability in a Clayey Soil As a Function of Feedstock and Pyrolysis Temperature. Environmental Science & Technology 46 (2012) 11770-11778.

[6] S.L. Goertzen, K.D. Thériault, A.M. Oickle, A.C. Tarasuk & H.A. Andreas, Standardization of the Boehm titration. Part I. CO_2 expulsion and endpoint determination. Carbon 48 (2010) 1252-1261.

[7] Z. Wang, G. Liu, H. Zheng, et al., Investigating the mechanisms of biochar's removal of lead from solution. Bioresource Technology 177 (2015) 308-317.

[8] W. Lewandowski, M. Kalinowska & H. Lewandowska, The influence of metals on the electronic system of biologically important ligands. Spectroscopic study of benzoates, salicylates, nicotinates and isoorotates. Review. Journal of inorganic biochemistry 99 (2005) 1407-1423.

[9] X.-H. Guan, G.-H. Chen & C. Shang, ATR-FTIR and XPS study on the structure of complexes formed upon the adsorption of simple organic acids on aluminum hydroxide. Journal of Environmental Sciences 19 (2007) 438-443.

[10] K. Mohammad, The use of various types of NMR and IR spectroscopy for structural characterization of chitin and chitosan, Chitin, Chitosan, Oligosaccharides and Their Derivatives. London: CRC Press, 2010. 149-170.

[11] S.K. Yong, N. Bolan, E. Lombi & W. Skinner, Synthesis and characterization of thiolated chitosan beads for removal of Cu(II) and Cd(II) from wastewater. Water, Air, & Soil Pollution 224 (2013) 1-12.

[12] B. Olu-owolabi, O. Pputu, K. Adebowale, O. Ogunsolu & O. Olujimi, Biosorption of Cd^{2+} and Pb^{2+} ions onto mango stone and cocoa pod waste: kinetic and equilibrium studies. Sci Res Essays 7 (2012) 1614-1629.

[13] N. Meunier, J. Laroulandie, J.F. Blais & R.D. Tyagi, Cocoa shells for heavy metal removal from acidic solutions. Bioresource Technology 90 (2003) 255-263.

[14] G. Issabayeva, M.K. Aroua & N.M.N. Sulaiman, Removal of lead from aqueous solutions on palm shell activated carbon. Bioresource Technology 97 (2006) 2350-2355.

[15] S. Abdel-Halim, A. Shehata & M. El-Shahat, Removal of lead ions from industrial waste water by different types of natural materials. Water Research 37 (2003) 1678-1683.

[16] G. Yuvaraja, N. Krishnaiah, M.V. Subbaiah & A. Krishnaiah, Biosorption of Pb (II) from aqueous solution by Solanum melongena leaf powder as a low-cost biosorbent prepared from agricultural waste. Colloids and Surfaces B: Biointerfaces 114 (2014) 75-81.

[17] M. Martínez, N. Miralles, S. Hidalgo, et al., Removal of lead (II) and cadmium (II) from aqueous solutions using grape stalk waste. Journal of Hazardous Materials 133 (2006) 203-211.

[18] S. Quek, D. Wase & C. Forster, The use of sago waste for the sorption of lead and copper. Water Sa 24 (1998) 251-256.

[19] M. Riaz, R. Nadeem, M.A. Hanif & T.M. Ansari, Pb (II) biosorption from hazardous aqueous streams using Gossypium hirsutum (Cotton) waste biomass. Journal of Hazardous Materials 161 (2009) 88-94.

[20] C.-C. Tay, A.-M. Muda, S. Abdul-Talib, M.-F. Ab-Jalil & N. Othman, The half saturation removal approach and mechanism of Lead (II) removal using eco-friendly industrial fish bone meal waste biosorbent. Clean Technologies and Environmental Policy 18 (2016) 541-551.

[21] B. Olu-Owolabi, O. Oputu, K. Adebowale, O. Ogonsolu & O. Olujimi, Biosorption of Cd2+ and Pb2+ ions onto mango stone and cocoa pod waste: kinetic and equilibrium studies. Sci. Res. Essays 7 (2012) 1614-1629.

[22] S.E. Samra, B. Jeragh, A.M. EL-Nokrashy & A.A. El-Asmy, Biosorption of Pb2+ from natural water using date pits: a green chemistry approach. Modern Chemistry & Applications (2014).