Adsorption efficiency of activated macadamia nutshell for the removal Organochlorine pesticides: Endrin and 4,4-DDT from aqueous solution

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Abstract

Many Organochlorine pesticides (OCPs) are currently used as pesticides have been of great concern due to their persistence, bioaccumulation as well as their toxicological effects on human health and the environment. The efficiency of activated macadamia nutshell as an adsorbent for removing pesticide mixture from the water was investigated.

The treated macadamia nutshell was characterized using fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM). Batch mode adsorption experiments were conducted by varying pH, concentration, adsorbent dose and contact time.

Pesticide removal was pH-dependent and found to be maximum at pH 2.0. The adsorption data were fitted to Langmuir, Freundlich, and Dubnin-Radushkevich (D-R) adsorption isotherm models. Experimental results showed that the Langmuir isotherm model best describes for the adsorption of endrin and 4,4-DDT. Pseudo-first order, pseudo-second order, and Weber-Morris equations were applied to fit the kinetic results.

The kinetics data for the adsorption process obeyed second-order rate equation. It was observed that 10 mg of activated macadamia could remove more than 91 % of endrin and 84 % 4,4-DDT from 10 ml of pesticide solution.

Keywords: Adsorption isotherms; Pesticides; Macadamia nutshell, Kinetics; Endrin, 4,4-DDT

INTRODUCTION:

Organochlorine pesticides (OCPs) are synthetic pesticides which are being used all over the world for many years. They belong to a group of molecules known as chlorinated hydrocarbon derivatives which have some application in the chemical industry and agriculture [1]. Many OCPs are currently used as pesticides have been of great concern due to their persistence, bioaccumulation as well as their toxicological effects on human health and the environment [2]. Pesticides are hazardous and toxic in nature and persist in the aquatic environment for many years after their application [3]. Most developed countries have banned the use of many of the pesticides due to their potential neurological effects to man and ecosystem. However, some people have continued to use them and sometimes in a disguised name. Environmental contamination by OCPs in water bodies have been a great concern, since most of these pesticide compounds are very persistent, bioaccumulative and their toxicity can pose harmful effects to human and ecosystems, because of their lipophilicity character and low chemical and biological degradation rates [4].

Many developing countries use various combination of many chemicals, biological and physical processes for decontamination of water. Adsorption as one of the processes has evolved almost effective physical methods for pesticide removal [5]. Adsorption is a surface based process in which adsorbate is held onto the surface of adsorbent by Van der Waals forces. It may also occur due to electrostatic attraction and chemical bonding. It is one of the well-known methods used in the removal of such hazardous compounds from polluted waters [6, 7].

The scientific community has focused on the quest for cheaper and more efficient materials to substitute the activated carbon (AC). Among the promising materials are the materials originated from vegetal biomass (leaves, root,

wood, seeds, etc.) [8]. Activated carbon in different forms (powder, granular, or brittle) has been employed over the years in the treatment of both industrial and municipal wastewater due to its ability to absorb a wide variety of both organic and inorganic compounds to non-detectable trace levels. Either chemical or physical activation can produce activated carbon, and it is common that oxidizing conditions are employed to impart the surface oxygen groups to the carbon [9], making the surface of the carbon acidic [10]. However, acidic groups, particularly carboxylic groups, tend to attract water molecules through H-bonding, forming water clusters thereby reducing adsorption efficiency of AC [11]. South Africa is the third largest producer of Macadamia in the world after Australia and Hawaii[12]. As the growth rate of Macadamia plantations steadily increases so also is the accumulation of Macadamia shells [12, 13]. There appears to be no real use for waste Macadamia shells except for road compaction in farms and as a source of heat.

The present study reports the application of macadamia nutshells for producing a cheaper and more effective adsorbent for the removal of 4,4-DDT and endrin from aqueous solutions. Also, this study will also determine the effect of acid treatment on the adsorption properties of macadamia nutshells and how this treatment affect its ability to remove 4,4-DDT and endrin from solution. The adsorbent was prepared and characterized by scanning electron microscopy (SEM), and Fourier transforms infrared spectroscopy (FT-IR) analyses. The effects of contact time, the initial concentration of 4,4-DDT and endrin, activated carbon dosage, temperature and initial solution pH were studied. The removal capacity of macadamia nutshell was studied by fitting the adsorption data to kinetic and isotherm models.

MATERIALS AND METHODS:

All reagents were of analytical and HPLC grade (Merck, South Africa). Anhydrous sodium sulphate, 99.5 % pure, was deactivated by drying in the muffle furnace at 400 °C for 3 h before use. All solvents were subjected to distillation three times before use and were in a range of 99.0 to 99.5 % pure. OCP standards were obtained from DWS research laboratory in Pretoria, South Africa. Kieselgel Merck Typ 77754, 70 to 230 mesh 100 µm were purchased from Sigma-Aldrich, South Africa. Analytical grade sulphuric acid was purchased from Merck. Macadamia nutshells was supplied by Eastern Produce Estates—SA (Pty) Ltd (Louis Trichardt, South Africa).

Characterization of macadamia nutshells:

The elemental composition of the raw and modified Macadamia nutshells was performed on a Thermo Flash 2000 series CHNS/O Organic Elemental Analyzer. The infrared absorption spectra was obtained with a Shimadzu Spectrum FT-IR spectrometer (Shimadzu, 8300, Japan). Surface topographical information was obtained by a surface morphological study in the field by electron Hitachi S-5200 scanning electron microscope (SEM). FTIR spectroscopy qualitatively detected the surface functional groups on the carbon samples. Macadamia nutshell samples were dried at about 105 °C for up to 12 hours before the FT-IR analyses. Spectra of activated carbons were obtained in a frequency band range from 4000 to 650 cm^{-1} using finely powdered KBr as a reference in a KBr/Carbon pellet (200:1 mass ratio).

Macadamia homogenization (sample preparation):

Macadamia nutshells were washed thoroughly with deionized water to remove dirt and then dried in the vacuum oven at 105 °C overnight. The shells were crushed and ground to a fine powder and then sieved through a pore size of between 90 and 150 µm. This sample was labelled as untreated Macadamia nutshell (UMN). The UMN sample was treated with 0.1 M HCl (Stirred for 3 h) to remove all the nutrients from the shells and labelled treated Macadamia nutshell (TMN). TMN was washed with deionized water through a funnel until the water coming out of funnel was neutral. The samples were then dried in a vacuum oven at 105 °C overnight.

Batch contact adsorption experiments:

The effects of various parameters on Endrin and DDT adsorption by activated macadamia nutshell were investigated using batch contact adsorption at 25 °C. These experiments were performed with 100.0 ml of OCP solution (initial concentration 20-100.0 mg L^{-1}), at different contact times (5.0 – 90.0 min), adsorbent dosage (1-12 g L^{-1}) and pH values (2.0 – 12.0). For adsorption equilibrium studies 10 mg adsorbent was placed in a series of conical flasks (150.0 mL) each one containing 100.0 mL of different initial OCP concentrations (20.0 – 100.0 mg L^{-1}) at pH 2.0. The conical flasks were shaken in a rotary orbital shaker at 150 rpm for 60.0 min.

The experiments were carried out in replicate (n = 3), and blanks were performed. The amount of OCP adsorbed per gram of adsorbate at equilibrium (qe), at any time (qt) and the OCP removal percentage (R) were obtained by the Eqs. (1) – (3), respectively:

$$q_e = \frac{C_0 - C_e}{m} V \qquad \text{.............. 1}$$

$$q_t = \frac{C_0 - C_t}{m} V \qquad \text{............... 2}$$

$$R = \frac{C_0 - C_e}{C_0} 100 \qquad \text{............... 3}$$

Where C_0 is the initial OCP concentration (mg L^{-1}), C_e is the equilibrium OCP concentration (mg L^{-1}), C_t is the OCP concentration at any time (mg L^{-1}), m is the adsorbent amount (g), and V is the volume of dye solution (L).

Adsorption isotherms and kinetic modelling:

The successful adsorption process depends on the kinetic parameters. Knowing the adsorption kinetics, it is possible to devise and conduct the process more efficiently. In order to relate the concentration of the adsorbate in the liquid and the amount adsorbed on the sorbent surface, several models have been used to describe these phenomena (Langmuir [14], Freundlich [15]; film diffusion model) and were fitted with the experimental data. Furthermore, it is known that equilibrium isotherms are essential towards an understanding of the interaction mechanism between OCP and adsorbent. To study the relationship between adsorbed OCP per unit of adsorbent (mg g^{-1}) and non-adsorbed OCP concentration in the aqueous phase (mg L^{-1}) at equilibrium, three equilibrium isotherms nominated Langmuir, Freundlich and film diffusion model were used. The kinetic and equilibrium parameters were determined by the fits on the models with the experimental data through nonlinear regression.

The Langmuir model assumes a monolayer coverage of a homogenous adsorbent surface by the adsorbate[14], and Langmuir isotherm equation is given below.

$$q_e = \frac{q_m K_1 C_e}{1 + K_1 C_e} \qquad \text{............ 4}$$

Where, q_e is the equilibrium sorbed concentration (in mg of adsorbate/g of sorbent), q_m (mg g^{-1}) is the adsorption capacity, C_e (mg L^{-1}) is the equilibrium solution phase concentration and k_1 (L mg^{-1}) is the affinity coefficient which is related to the energy of adsorption. The dimensionless parameter, R_L, also known as the equilibrium parameter or separation factor is given by Eq. 4 was calculated and used to interpret adsorption conditions from the Langmuir isotherm.

$$R_L = \frac{1}{1 + bC_0} \qquad \text{......... 5}$$

Where b is the Langmuir constant and C_0 is the highest initial pesticide concentration (mg L^{-1}). The value of R_L indicates the type of isotherm namely, unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The Freundlich model relates the sorption of adsorbate to heterogeneous surfaces, and it assumes multilayer adsorption[15]. The equation is given below.

$q_e = K_f C_e^{(1/n)}$ 6

Where, q_e is the equilibrium sorbed concentration (mg of adsorbate/g of sorbent) and C_e (mg L^{-1}) is the equilibrium solution phase concentration. K_f is the Freundlich constant related to the adsorption capacity, and 1/n is the intensity of adsorption.

Several kinetic models are used to investigate the processes controlling biosorption of adsorbate as well as the rate of mass transfer. Pseudo-first order (PFO) and pseudo second order (PSO) were employed to fit the experimental data. The equations for the models in their non-linearized form are given below.

The PFO rate equation (also, known as Lagergren equation) and the PSO kinetic model [16] are represented in Eqs. 7 and 8.

$$\text{Log} (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad .... 7$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad .... 8$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg g^{-1}) and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}), q_e is obtainable by a linear regression analysis of the $t / q_t = f (t)$ function.

The equation proposed to govern the film diffusion controlled adsorption process is given by:

$$\ln \left\{ \frac{C}{C_0} \right\} = - K_s \frac{S_s}{V} t \quad .... 9$$

Where k_s is the diffusion coefficient in m/s, S_s is the external adsorbent surface area in m^2, t is time in seconds, and V is the solution volume in m^3.

RESULTS AND DISCUSSION
Characterization of the adsorbent:
The infrared spectroscopy technique was used to identify the functional groups on the macadamia nutshell which can be responsible for binding OCP molecules, and to elucidate the OCP–adsorbent interactions.

The TMN spectra before adsorption showed similar characteristics except for differences caused by the treatments. A wide absorption band at 3000 – 3500 cm^{-1} was observed for spectra of MAC before adsorption with a maximum at about 3255 cm^{-1} is assigned to O–H stretching vibrations of hydrogen-bonded hydroxyl groups [17]. Aliphatic C–H stretching vibration is found as a very weak peak at 2845 cm^{-1} while asymmetric vibration of CH$_2$ group appears at 2926 cm^{-1} (Figure 1).

A broad asymmetric band further characterized the spectra of MAC before adsorption at 1621 cm^{-1} ascribed to the presence of carboxylate group [18, 19]. The broadband decreased in intensity after pesticides loading signifying its involvement in OCPs removal. The shoulder at 1038 cm^{-1} can be ascribed to C–OH stretching of phenolic groups [20]. The differences observed in FTIR spectra of MAC before and after adsorption of OCPs confirm the participation of functional groups in the removal of OCPs by macadamia nutshell.

Surface morphology of activated carbon:
Scanning electron microscopy (SEM) was used to observe the surface physical morphology of the sample.

The morphology and structure of treated macadamia before adsorption was characterized by scanning electron microscope (SEM), and the micrographs are shown in Figure 2. The SEM image revealed that the material consisted of flaky long fold-like structure (Figure 2) which are typical of plant materials. The structural backbone of the material was not greatly altered since they retained their flakiness, suggesting that the treatment was not excessively harsh to destroy the material. The porosity of the material is evident in interconnected networks. A closer look at the surface shows that pores are elongated which confirmed that macadamia retained the structure of lignocellulose-based plant materials proving that the activation process removed more of the non-carbon materials [21].
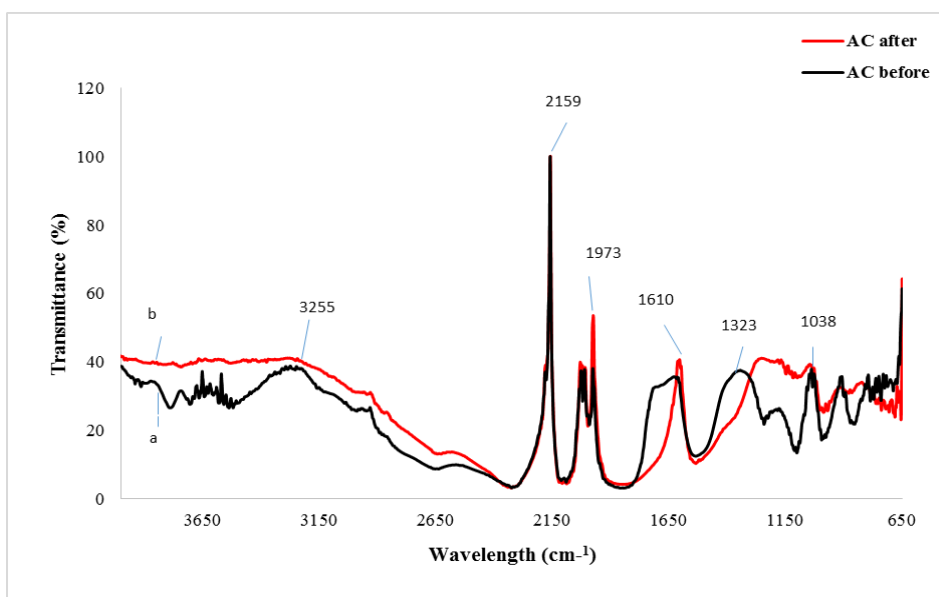

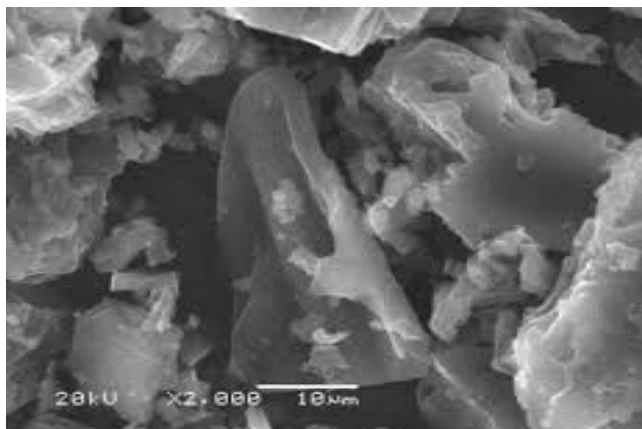**Figure 1. FTIR spectra of TMN before and after adsorption of the pesticide.**

Figure 2. SEM micrograph of treated macadamia nutshell (TMN)

Effect of pH:

Several studies have reported that pH of the solution is a critical factor in adsorption from solution [22]. The variations of the pH do not only change carbon surface properties, but this parameter can also affect the state of the ionic species in solution. The adsorption capacity of adsorbents was found to be pH-dependent as shown in Figure 3. An increase in pH from 2 - 12 resulted in a decrease in adsorption from 103.30 to 55.60 mg g^{-1} for 4,4-DDT and 106 to 52.90 mg g^{-1} for endrin. The pH dependence of the adsorption process can largely be related to the type and ionic state of functional groups present on the adsorbents and compound speciation in solution. Maximum adsorption of pesticides occurs at pH 2, and hence that value was selected as the optimum and used throughout the study.
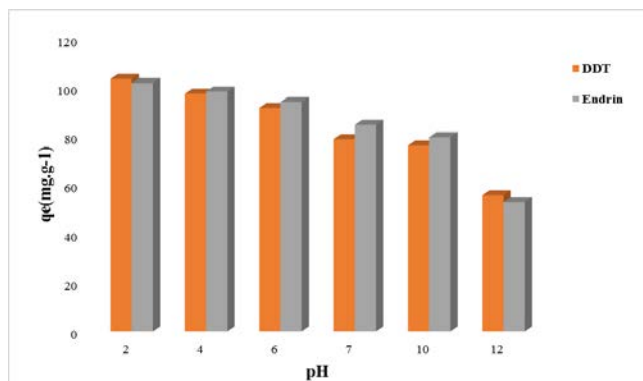

Figure 3. Effect of pH on the removal of 4,4-DDT and endrin by TMN

Effect of adsorbent dose:

The percentage removal of the pesticide: 4,4-DDT and endrin with adsorbent dose ranged from 1 to 12 g L^{-1} for adsorption is displayed in Figure 4. The adsorbent dose significantly influences the amount of pesticide adsorbed. Initially, the amount of 4,4-DDT adsorbed was found to be rapid from 1-12 g L^{-1}, a further increase of adsorbent dose resulted in much less increase in adsorption, and hence 10 g L^{-1} was considered the optimum dose. The initial rise in adsorption with adsorbent dose is probably due to stronger driving force with a rise in adsorbent dose; there is a less commensurate increase in adsorption resulting from lower adsorptive utilization of adsorbent [23]. In case of endrin, the difference between the percentage removal of endrin and adsorption is lower at the start of the experiment (at about one hour) but gradually increases and then remains constant.

The percentage (%) removal of 4,4-DDT and endrin reaches its optimal value at the dose of around 10 g L^{-1}, adsorption is lower at the start of the experiment (at about one hour) but gradually increases and then remains constant. From the adsorption processes, it seems that the adsorption of endrin dominates at the initial stage and bio-sorption dominates after reaching adsorption equilibrium. The removal of 4,4-DDT was 86 and 91 % for adsorption and endrin respectively.
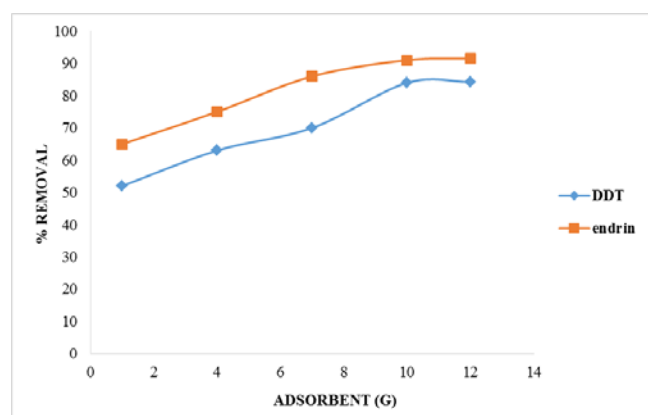

Figure 4. Effect of adsorbent dose on 4,4-DDT and endrin removal by TMN

Effect of initial concentration and contact time:

The rate of 4,4-DDT uptake on activated macadamia as evident from Figure 5 depicts that the sorption is quite rapid initially, gradually slows down and then reaches the equilibrium. Equilibrium was attained at 60 min, and no significant change was observed after equilibrium time. At equilibration time, adsorption was unaffected by initial concentration, but rather the amount adsorbed increased with increasing concentration of the pesticides.
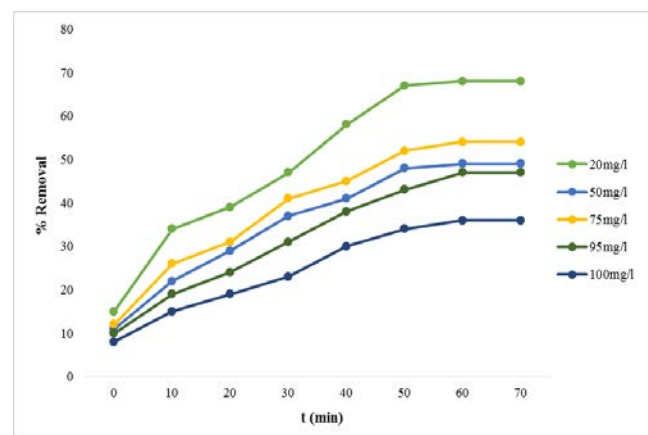

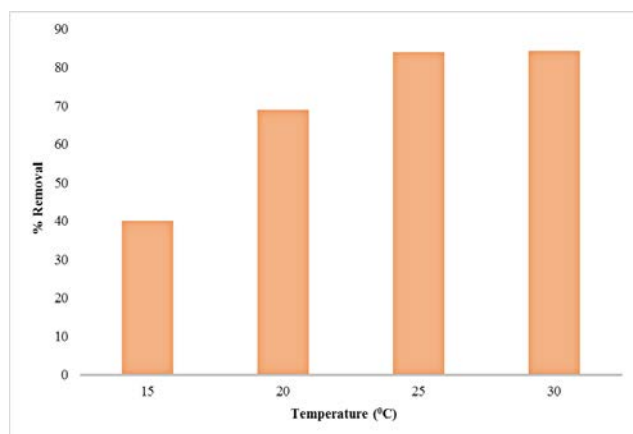**Figure 5. Effect of initial concentration of 4,4-DDT removal by TMN**

Figure 6. Effect of different temperatures of 4,4-DDT removal onto macadamia

Effect of temperature:

It was observed that adsorption capacity of activated carbon decreased from 16.90 to 8.00 mg g^{-1} with an increase in temperature from 20 °C to 30 °C (Figure 6). Gupta et al. [24] have reported that temperature increase effect on the adsorption properties may be due to the tendency for the target molecules to escape from the solid phase to the bulk phase with an increase in temperature of the solution [24]. A similar observation was also reported in the study on the sorption of acid dye by activated clay and activated carbon [25].

CONCLUSION

The non-competitive adsorption of 4,4-DDT and endrin, as representatives of pesticides, onto macadamia from aqueous phase has been studied regarding kinetics and equilibrium isotherms. Activated carbon samples were prepared under specific conditions to evaluate the effect of varying adsorbent properties on the studied pesticides' adsorption and the performance of macadamia. The study gave an insight into the use of treated macadamia as a low-cost adsorbent for pesticide removal from aqueous solutions, since 10 mg of activated macadamia was able to remove more than 91 % of endrin and 84 % for 4,4-DDT from 10 ml of pesticide solution. The Langmuir, Freundlich and D-R isotherms are found to be applicable in the present pesticide mixture adsorption, which may be attributed to the formation of a monolayer on the surface of the adsorbent. Endrin and 4,4- DDT fitted comparatively well in Langmuir isotherm. Different kinetic models used to fit experimental data showed that the results best describe the Pseudo-second order model for the adsorption of endrin and 4,4-DDT on treated macadamia nutshell in comparison to the pseudo-first-order model. These results demonstrate that macadamia, which is easily available, could be an effective and low-cost adsorbent for the removal of pesticides from the aqueous solutions.

REFERENCES

[1] Ravindran, J., Pankajshan, M. and Puthur, S. (2016). Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdiscip. Toxicol.*, 9(3-4): 90–100. DOI: 10.1515/intox-2016-0012.

[2] Monirith, I., Uneno, D. and Takahashi, S. et al. (2003). Asia-Pacific mussel watch: monitoring contamination of persistent organochlorine compounds in coastal waters of Asian countries. *Mar. Pollu. Bull.*, 46(3): 281–300. DOI: 10.1016/S0025-326X(02)00400-9.

[3] Radan, B.D., Pennigton, D.W. and Eckley, N. et al. (1999). Screening for persistent organic pollutants: Techniques to provide a scientific basis for pops criteria in international negotiations. *Environ. Sci. Technol.*, 33(20): 3482–3488. DOI: 10.1021/es980060t.

[4] Barakat, A.O., Kim, M. and Qian, Y. et al. (2002). Organochlorine pesticides and PCB residues in sediments of Alexandria Harbour, Egypt. *Baseline/Mar. Pollut. Bull.*, 44: 1421–1434. DOI: 10.1016/S0025-326X(02)00313-2.

[5] Zhang, S.J., Shao, T. and Bekaroglu, S.S.K. et al. (2009). The impacts of aggregation and surface chemistry of carbon nanotubes on the adsorption of synthetic organic compounds. *Environ. Sci. Technol.*, 43(15): 5719–5725. DOI: 10.1021/es900453e.

[6] Sheha, R.R. and Metwally, E. (2009). Equilibrium isotherm modelling of cesium adsorption onto magnetic materials. *J. Hazard. Mater.*, 143(1-2): 354–361. DOI: 10.1016/j.jhazmat.2006.09.041.

[7] Gupta, V.K., Jain, C.K. and Ali, I. et al. (2002). Removal of lindane and malathion from waste water using baggage fly ash — a sugar industry waste. *Water Res.*, 36(10): 2483–2490. DOI: 10.1016/S0043-1354(01)00474-2.

[8] Sharma, P., Kaur, H. and Sharma, M. et al. (2011). A review on applicability of naturally available adsorbents for the removal of hazardous dyes from aqueous waste. *Environ. Monit. Assess.*, 183(1-4): 151–195. DOI: 10.1007/s10661-011-1914-0.

[9] Sheng, G.D., Shao, D.D. and Ren, X.M. et al. (2010). Kinetics and thermodynamics of adsorption of ionizable aromatic compounds from aqueous solutions by as-prepared and oxidized multiwalled carbon nanotubes. *J. Hazard. Mater.*, 178(1-3): 505–516. DOI: 10.1016/j.jhazmat.2010.01.110.

[10] Liu, S. and Wang, R. (2011). Modified activated carbon with an enhanced nitrobenzene adsorption capacity. *J. Porous Mater.*, 18(1): 99–106. DOI: 10.1007/s10934-010-9360-x.

[11] Velasco, L.F. and Ania, C.O. (2011). Understanding phenol adsorption mechanisms on activated carbons. *Adsorption*, 17(1): 247–254. DOI: 10.1007/s10450-011-9322-x.

[12] Mogala, M. (2016). A profile of the South African macadamia nuts market value chain 2016. Department of Agriculture, Forestry and Fisheries, Pretoria, South Africa.

[13] Moodley, R., Kindness, A. and Jonnalagadda, S. (2007). Chemical composition of edible *Macadamia* nuts (*Macadamia integrifolia*) and impact of soil quality. *J. Environ. Sci. Health A Tox. Hazard Subst. Environ. Eng.*, 42(14): 2097–2104. DOI: 10.1080/10934520701627074.

[14] Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, 40(9): 1361–1403. DOI: 10.1021/ja02242a004.

[15] Freundlich, H. and Helle, W. (1939). The Adsorption of *cis-* and *trans*-Azobenzene. *J. Am. Chem. Soc.*, 61(8): 2228–2230. DOI: 10.1021/ja01877a071.

[16] Ho, Y.S. and McKay, G. (1998). Sorption of dye from aqueous solution by Peat. *Chem. Eng. J.*, 70(2): 115–124. DOI: 10.1016/S0923-0467(98)00076-1.

[17] Valente Nabais, J.M., Laginhas, C.E.C. and Carrott, P.J.M. et al. (2011). Production of activated carbons from almond shell. *Fuel Process. Technol.*, 92(2): 234–240. DOI: 10.1016/j.fuproc.2010.03.024.

[18] Yang, L. and Chen, J.P. (2008). Biosorption of hexavalent chromium onto raw and chemically modified *Sargassum sp*. *Bioresour Technol.*, 99(2): 297–307. DOI: 10.1016/j.biortech.2006.12.021.

[19] González Bermúdez, Y.; Rodríguez Rico, I.L. and Guibal, E.E. et al. (2012). Biosorption of hexavalent chromium from aqueous solution by *Sargassium muticum* brown alga. Application of

statistical design process optimization. *Chem. Eng. J.*, 183: 68–76. DOI: 10.1016/j.cej.2011.12.022.

[20] Figueiredo, J.L., Pereira, M.F.R. and Freitas, M.M.A. et al. (1999). Modification of the surface chemistry of activated carbons. *Carbon*, 37: 1379–1389. DOI: 10.1016/S0008-6223(98)00333-9

[21] Rincon-Silva, N.G., Moreno-Pirajan, J.C. and Giraldo, L. (2016). Equilibrium, kinetics and thermodynamics study of phenols adsorption onto activated carbon obtained from lignocellulosic material (*Eucalyptus Globulus labill* seed). *Adsorption*, 22(1): 33–48. DOI: 10.1007/s10450-015-9724-2.

[22] Budinova, T., Savova, D. and Tsyntsarski, B. et al. (2009). Biomass waste-derived activated carbon for the removal of arsenic and manganese ions from aqueous solutions. *Appl. Surf. Sci.*, 255(8): 4650–4657. DOI: 10.1016/j.apsusc.2008.12.013.

[23] Raghuvanshi, S.P., Singh, R. and Kaushi, C.P. (2004). Kinetics study of methylene blue dye bio-adsorption on bagasse. *Appl. Ecol. Env. Res.*, 2(2): 35–43. DOI: 10.15666/aeer/03035043.

[24] Gupta, V.K., Mohan, D. and Sharma, S. (1998). Removal of lead from wastewater using bagasse fly ash—a sugar industry waste material. *Sep. Sci. Technol.*, 33(9): 1331–1343. DOI: 10.1080/01496399808544986.

[25] Ho, Y.S. and Chiang, C.C. (2001). Sorption studies of acid dye by mixed sorbents. *Adsorption*, 7(2): 139–147. DOI: 10.1023/A:1011652224816.