

REFERENCE

- Abdel-Ghani, N. T., G. A. El-Chaghaby & E. M. Zahran. 2015. "Pentachlorophenol (PCP) adsorption from aqueous solution by activated carbons prepared from corn wastes." *International Journal of Environmental Science and Technology* 12: 211–222. doi:10.1007/s13762-013-0447-1.
- Abechi, S. E., C. E. Gimba, A. Uzairu & Y. A. Dallatu. 2013. "Preparation and Characterization of Activated Carbon from Palm Kernel Shell by Chemical Activation". *Research Journal of Chemical Science*. Vol. 3, (7): p. 54-61.
- Acharya, J., J. N. Sahu, B. K. Sahoo, C. R. Mohanty & B. C. Meikap. 2009. "Removal of Chromium (VI) from Wastewater by Activated Carbon Developed from *Tamarind wood* Activated with Zinc Chloride". *Chemical Engineering Journal*. Vol. 150, (1): p. 25-39.
- Achaw, O. W. 2012. A Study of the Porosity of Activated Carbons Using the Scanning Electron Microscope. *Scanning Electron Microscopy*. Kazmiruk, V. InTech, Rijeka.
- Adegoke, K. A. & O. S. Bello. 2015. "Dye Sequestration Using Agricultural Wastes as Adsorbents". *Water Resources and Industry*. Vol. 12: p. 8-24.
- Adeyeye, E. I. 2015. "Proximate, Mineral and Antinutrient Compositions of Natural Cocoa Cake, Cocoa Liquor and Alkalized Cocoa Powders" *Journal of Advanced Pharmaceutical Science and Technology*. Vol. 1 (3): p. 1-12.
- Adinata, D., W. M. A. Wan Daud & M. K. Aroua. 2007. "Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3 ". *Bioresource Technology*. Vol. 98: p. 145–149.
- Afoakwa, E. O., J. Quao, J. Takrama, A. S. Budu & F. K. Saalia. 2011. "Chemical Composition and Physical Quality Characteristics of Ghanaian Cocoa Beans as Affected by Pulp Pre-Conditioning and Fermentation". *Journal of Food Scientists & Technologists*. Vol. 50, (6): p. 1097–1105.
- Ahiduzzaman, M. & A. K. M. Sadrul Islam. 2016. "Preparation of Porous Bio-Char and Activated Carbon from Rice Husk by Leaching Ash and Chemical Activation". *SpringerPlus*, 5: 1248.
- Ahmad, M. A. & R. Alrozi. 2010. "Optimization of Preparation Conditions for Mangosteen Peel-Based Activated Carbons for the Removal of Remazol Brilliant Blue R Using Response Surface Methodology". *Chemical Engineering Journal*. Vol. 165, (3): p. 883–890.
- Ahmad, M. A. & R. Alrozi. 2011. "Removal of Malachite Green Dye from Aqueous Solution Using Rambutan Peel-Based Activated Carbon- Equilibrium, Kinetic and Thermodynamic Studies". *Chemical Engineering Journal*. Vol. 171: p. 510– 516.

Ahmad, A.A., B.H. Hameed & A.L. Ahmad. 2009. "Removal of Disperse Dye from Aqueous Solution using Waste-derived Activated Carbon: Optimization Study". *Journal of Hazardous Materials*. Vol. 170 : p. 612–619.

Ahmad, M. A. & N. K. Rahman. 2011. "Equilibrium, Kinetics and Thermodynamic of Remazol Brilliant Orange 3R Dye Adsorption on Coffee Husk-Based Activated Carbon". *Chemical Engineering Journal*. Vol. 170: p. 154-161.

Ahmad, F., W. M. A. Wan Daud, M. A. Ahmad & R. Radzi. 2011. "Using Cocoa (*Theobroma cacao*) Shell-Based Activated Carbon to Remove 4-Nitrophenol From Aqueous Solution Kinetics and Equilibrium Studies". *Chemical Engineering Research and Design*. Vol. 178: p. 461–467.

Ahmad, F., W. M. A. Wan Daud, M. A. Ahmad & R. Radzi. 2012. "Cocoa (*Theobroma cacao*) Shell-based Activated Carbon by CO₂ Activation in Removing of Cationic Dye from Aqueous Solution: Kinetics and Equilibrium Studies". *Chemical Engineering Research and Design*. Vol. 90: p. 1480–1490.

Ahmad, F., W. M. A. Wan Daud, M. A. Ahmad, R. Radzi & A. A. Azmi. 2013a. "The Effects of CO₂ Activation, on Porosity and Surface Carbon from *Theobroma cacao* – Shell Based Activated Carbon." *British Journal of Applied Science & Technology*. Vol. 1: p. 5021-5044.

Ahmad, F., W. M. A. Wan Daud, M. A. Ahmad & R. Radzi. 2013b. "The Effects of Acid Leaching on Porosity and Surface Functional Groups of Cocoa (*Theobroma cacao*) – Shell Based Activated Carbon." *Chemical Engineering Research and Design*. Vol. 91: p. 1028–1038.

Ahmad, M. A., N. A. A. Puad & O. S. Bello. 2014. "Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by microwave-induced KOH activation." *Water Resources and Industry* 6: 18-35. doi:<https://doi.org/10.1016/j.wri.2014.06.002>.

Aji, M. M., B. Gutti & B. K. Highina. 2015. "Production and Characterization of Activated Carbon from Groundnut Shell Sourced in Maiduguri." *Columban Journal of Life Science* 17 (1): 18-24.

Ajifack, D. L., J. N. Ghogomu, T. D. Noufame, J. N. Ndi & J. M. Ketcha. 2014. "Adsorption of Cu (II) Ions from Aqueous Solution onto Chemically Prepared Activated Carbon from *Theobroma cacao*". *British Journal of Applied Science & Technology*. Vol. 4, (36): p. 5021-5044.

Akinnuli, B. O., S. P. Ayodeji & A. J. Omeiza. 2014. "Computer Aided Design for Cocoa Beans Processing Yield Prediction". *International Journal of Applied Science and Technology*. Vol. 4, (5): p. 82-91.

Akinnuli, B. O., O. S. Bekunmi & C. O. Osueke. 2015. "Design Concepts towards Cocoa Wining Mechanization for Nibs Production in Manufacturing Industries". *British Journal of Applied Science & Technology*. Vol. 8, (1): p. 35-45.

Akpomie, K. G., F.A. Dawodu & K. O. Adebowale. 2015. "Mechanism on the sorption of heavy metals from binary-solution by a low cost montmorillonite and its desorption potential." *Alexandria Engineering Journal* 54 (3): 757-767. doi:<https://doi.org/10.1016/j.aej.2015.03.025>.

Al-Degs, Y.S., R. Abu-El-Halawa & S. S. Abu-Alrub. 2012. "Analyzing Adsorption Data of Erythrosine Dye Using Principal Component Analysis". *Chemical Engineering Journal*. Vol. 191: p. 185-194.

Al-Ghouthi, M. A. & Y. S. Al-Degs. 2014. "Manganese-Loaded Activated Carbon for the Removal of Organosulfur Compounds from High-Sulfur Diesel Fuels". *Energy Technology*. Vol. 2: p. 802-810.

Al-Qodah, Z & R. Shawabkah. 2009. "Production and Characterization of Granular Activated Carbon from Activated Sludge". *Brazilian Journal of Chemical Engineering*. Vol. 26, (1): p. 127-136.

Alabadi, A., S. Razzaque, Y. Yang, S. Chen & B. Tan. 2015. "Highly Porous Activated Carbon Materials from Carbonized Biomass with high CO₂ Capturing Capacity". *Chemical Engineering Journal*. Vol. 281: p. 606-612.

Allwar. 2012. "Characteristics of Micro- and Mesoporous Structure and Surface Chemistry of Activated Carbons Produced by Oil Palm Shell". *International Conference on Chemical, Ecology and Environmental Sciences*. Bangkok: n.d. p. 138-141.

Alslaibi, T. M., I. Abustan, M. A. Ahmad & A. A. Foul. 2012. "A Review: Production of Activated Carbon from Agricultural Byproducts via Conventional and Microwave Heating". *Journal of Chemical Technology & Biotechnology*. Vol. 88: p. 1183-1190.

Altenor, S., B. Carene, E. Emmanuel, J. Lambert, J. J. Ehrhardt & S. Gaspard. 2009. "Adsorption Studies of Methylene Blue and Phenol onto Vetiver Roots Activated Carbon Prepared by Chemical Activation". *Journal of Hazardous Materials*. Vol. 165: p. 1029-1039.

Alvarez-Urriarte, J. I., U. Iriarte-Velasco, N. Chimeno-Alanís & J. R. González-Velasco. 2014. "Application of Principal Component Analysis to the Adsorption of Natural Organic Matter by Modified Activated Carbons". *Separation Science and Technology*. Vol. 46: p. 2239-2249.

Angel. 2017. Staining Basics. Accessed July 23, 2017. https://online.science.psu.edu/micrb106_wd/node/6069.

Anovitz, L. M. & D. R. Cole. 2015. "Characterization and Analysis of Porosity and Pore Structures". *Reviews in Mineralogy & Geochemistry*. Vol. 80: p. 61-164.

Aprotosoae, A. C., S. V. Luca & A. Miron. 2016. "Flavor Chemistry of Cocoa and Cocoa Products — an Overview". *Comprehensive Reviews in Food Science and Food Safety*. Vol. 15: 73-91.

Arias, M., E. López, A. Nuñez, D. Rubinos, B. Soto, M. T. Barral & F. Díaz-Pierros. 1999. "Adsorption of Methylene Blue by Red Mud, An Oxide- Rich Byproduct of Bauxite Refining" In *Effect of Mineral-Organic-Microorganism Interactions on Soil and Freshwater Environments*, by J. Berthelin, P. M. Huang, J.-M. Bollag and F. Andreux, edited by J. Berthelin, P. M. Huang, J.-M. Bollag and F. Andreux, 361-365. New York: Springer US.

Asadullah, M., M. Asaduzzaman, M. S. Kabir, M. G. Mostafa & T. Miyazawa. 2010. "Chemical and Structural Evaluation of Activated Carbon Prepared from Jute Sticks for Brilliant Green Dye Removal from Aqueous Solution". *Journal of Hazardous Materials*. Vol. 174, (1-3): p. 437-443.

Aworn, A., P. Thiravetyan & W. Nakbanpote. 2008. "Preparation and Characteristics of Agricultural Waste Activated Carbon by Physical Activation Having Micro- and Mesopores". *Journal of Analytical and Applied Pyrolysis*. Vol. 82, p. 279-285.

Ayawei, N., A. N. Ebelegi & D. Wankasi. 2017. "Modelling and Interpretation of Adsorption Isotherms". *Hindawi Journal of Chemistry*. Vol. 2017: p. 1-11.

Bartel, J., J. Krumsiek & F. J. Theis. 2013. "Statistical Methods for the Analysis of High-Throughput Metabolomics Data." *Computational and Structural Biotechnology Journal* 4 (5): e201301009. doi:<https://doi.org/10.5936/csbj.201301009>.

Bashir, M. J. K., N. Ibrahim, M. N. Ismail & M. A. T. Jaya. 2015. "Physical Treatment Technologies for Landfill Leachate: Performance and Limitation." In *Control and Treatment of Landfill Leachate for Sanitary Waste Disposal*, by H. A. Aziz and S. A. Amr, 250-285. PA, USA: IGI Global.

Bello, U. S. & M. A. Ahmad. 2011. "Response Surface Modeling and Optimization of Remazol Brilliant Blue Reactive Dye Removal Using Periwinkle Shell-Based Activated Carbon". *Separation Science and Technology*, Vol. 46, (15): p. 2367-2379.

Bhatnagar, A., Hogland, W. M. Marques & M. Sillanpaa. 2013. "An Overview of the Modification Methods of Activated Carbon for Its Water Treatment Applications". *Chemical Engineering Journal*. Vol. 219: p. 499-511.

Beaumont, E. 1985. *Industrial Charcoal Making*. Rome: FAO Forestry Department.

Boehm, H. P. 2002. "Surface Oxides on Carbon and Their Analysis: A Critical Assessment". *Carbon*. Vol. 40, (2): p. 145-149.

Bohli, T., N. Fiol, I. Villaescusa & A. Ouedemi. 2013. "Adsorption on activated carbon from olive stones: kinetic and equilibrium of phenol removal from aqueous solution". *Journal of Chemical Engineering & Process Technology*. Vol. 4, (6): p. 1-5.

Bonvin, F., L. Jost, L. Randin, E. Bonvin & T. Kohn. 2016. "Super-Fine Powdered Activated Carbon (SPAC) for Efficient Removal of Micro-Pollutants from Wastewater Treatment Plant Effluent". *Water Research*. Vol. 90: p. 90-96.

Brennan, J. K., T. J. Bandosz, K. T. Thomson & K. E. Gubbins. 2001. "Water in Porous Carbons". *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. Vol. 187-188: p. 539-568.

Bulut, E., M. Ozacar & I. A. Sengil. 2008. "Adsorption of Malachite Green onto Bentonite: Equilibrium and Kinetic Studies and Process Design". *Microporous and Mesoporous Materials*. Vol. 115: p. 234-246.

Cabal, B. C. O. Ania, J. B. Parra & J. J. Pis. 2009. "Kinetics of Naphthalene Adsorption on an Activated Carbon: Comparison between Aqueous and Organic Media. *Chemosphere*. Vol. 76, (4): p. 433-438.

Cadbury. 2017. "Cocoa Growing Countries". Cadbury. <<https://www.cadbury.com.au/About-Chocolate/Cocoa-Growing-Countries.aspx>>. Accessed 22 April 2017.

Cao, Z., G. Liu, H. Zhan, C. Li, Y. You, C. Yang & H. Jiang. 2016. "Pore Structure Characterization of Chang-7 Tight Sandstone Using MICP Combined with N₂GA Techniques and Its Geological Control Factors". *Scientific Reports*. Vol. 6: p. 1-13.

Chandra, T. C., M. M. Mirna, J. Sunarso, Y. Sudaryanto & S. Isnadji. 2009. "Activated Carbon from Durian Shell: Preparation and Characterization". *Journal of Taiwan Institute Chemical Engineering*. Vol. 40: p. 457-462.

Chayande, P. K., S.P. Singh & M. K. N. Yenkie. 2013. "Characterization of Activated Carbon Prepared from Almond Shells for Scavenging Phenolic Pollutants". *Chemical Science Transaction*. Vol. 2, (3): p. 835-840.

Chen, Y., Y. Zhu, Z. Wang, Y. Li, L. Wang, L. Ding, X. Gao, Y. Ma & Y. Guo. 2011. "Application Studies of Activated Carbon Derived from Rice Husks Produced by Chemical-Thermal Process—A Review". *Advances in Colloid and Interface Science*. Vol. 163, (1): p. 39-52.

Chen, D., H. Feng & J. Li. 2012. "Graphene Oxide: Preparation, Functionalization, and Electrochemical Applications." *Chemical Reviews* 112: 6027-6053. doi:dx.doi.org/10.1021/cr300115g.

Chethana, K. P. 2014. "A Research on Cocoa Pod Husk Activated Carbon for Textile Industrial Wastewater Colour Removal". *International Journal of Research in Engineering and Technology*. Vol. 3, (3): p. 731-737.

Choo, H. S., L. C. Lau, A. R. Mohamed & K. T. Lee. 2013. "Hydrogen Sulfide Adsorption by Alkaline Impregnated Coconut Shell Activated Carbon". *Journal of Engineering Science and Technology*. Vol. 8, (6): p. 741 - 753.

Cousland, B. 2017. "Gas Cleaning Active Carbon Systems". *Begg Cousland*. <<http://beggcousland.co.uk/products/gas-cleaning/active-carbon-systems/>>. Accessed 5 February 2017.

Cruz, G., M. Pirlä, M. Huuhtanen, L. Carrión, E. Alvarenga & R. L. Keiski. 2012. "Production of Activated Carbon from Cocoa (*Theobroma cacao*) Pod Husk". *Civil & Environmental Engineering*. Vol. 2, (2): p. 1-6.

Dada, A.O, A.P Olalekan, A.M Olatunya & O Dada. 2012. "Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn 2+ Unto Phosphoric Acid Modified Rice Husk". *IOSR Journal of Applied Chemistry*. Vol. 3, (1): p. 38-45.

Danewalia, S. S., G. Sharma, S. Thakur & K. Singh. 2016. "Agricultural wastes as a resource of raw materials for developing low-dielectric glass-ceramics." *Scientific Reports* 6 (24617). doi:<https://doi.org/10.1038/srep24617>.

Dawood, S. & T. K. Sen. 2014. "Review on Dye Removal from Its Aqueous Solution into Alternative Cost Effective and Non-Conventional Adsorbents". *Journal of Chemical and Process Engineering*. Vol. 1: p. 1-11.

Demiral, H. & G. Gündüzoğlu. 2010. "Removal of Nitrate from Aqueous Solutions by Activated Carbon Prepared from Sugar Beet Bagasse". *Bioresource Technology*. Vol. 101, (6): p. 1675-1680.

Demirbas, A. 2009. "Agricultural Based Activated Carbons for the Removal of Dyes from Aqueous Solutions: A Review". *Journal of Hazardous Materials*. Vol. 167: p. 1-9.

Desta, M. B. & A. Lucia. 2013. "Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (*Eragrostis tef*) Agricultural Waste". *Journal of Thermodynamics*. Vol. 2013: p. 1-6. doi:10.1155/2013/375830.

Dinç, I., M. Sıqdel, S. Dinç, M. S. Sıqdel, M. L. Pusey & R. S. Aygün. 2014. "Evaluation of Normalization and PCA on the Performance of Classifiers for Protein Crystallization Images". *SOUTHEASTCON 2014*, IEEE: Lexington, KY, USA.

Dufek, M. & M. Hayles. 2003. "The Quanta FEG 200, 400, 600 User's Operation Manual". University of Nebraska-Lincoln College of Engineering. <<http://engineering.unl.edu/downloads/files/UserManual-Quanta200SEM-sm.pdf>>. Accessed 4 May 2016.

Dunne, C., B. Dolan & M. Clyne. 2014. "Factors that mediate colonization of the human stomach by *Helicobacter pylori*." *World Journal of Gastroenterology* 20 (19): 5610–5624. doi:10.3748/wjg.v20.i19.5610.

Egwim, C. E., A. M. Halima & H. O. Ibrahim. 2013. "Purification of Frog Oil Using Animal Bone-Base Activated Carbon". *International Journal of Emerging Technology and Advanced Engineering*. Vol. 3 (3): p. 983-987.

Elementar. 2017. "Data Bulletin - CHN analysis in coal and fly ash using the vario MACRO cube". elementar.

http://www.elementar.de/fileadmin/user_upload/Elementar_Website/Downloads/Data_Bulletins/vario_MACRO_cube/DB-CHN-analysis-in-coal-and-fly-ash-using-the-vario-MACRO-cube.pdf.

El-Hendawy, A. N. A. 2006. "Variation in the FTIR spectra of a biomass under impregnation, carbonization and oxidation conditions". *Journal of Analytical and Applied Pyrolysis*. Vol. 75: p. 159-166.

El-Sayed, G. O., M. M. Yehia & A. A. Asaad. 2014. "Assessment of Activated Carbon Prepared from Corncob by Chemical Activation with Phosphoric Acid". *Water Resources and Industry*. Vol. 7-8: p. 66-75.

Eza, T. S. M., W. Y. Wan Ahmad, M. R. Ahmad, K. Omar & M. N. Ahmad. 2014. "Effectiveness of Activated Carbon Produced From Coconut and Oil Palm Shells as Anti-Odour on Textile Fabrics". *Indian Journal of Fibre & Textile Research*. Vol. 39: p. 190-195.

Fałtynowicz, H., J. Kaczmarczyk & M. Kułczyński. 2015. "Preparation and characterization of activated carbons from biomass material – giant knotweed (*Reynoutria sachalinensis*).". *Open Chem*. 13: 1150–1156. doi:10.1515/chem-2015-0128.

Ferreira, R. C., O. M. Couto Junior, K. Q. Carvalho, P. AnArroyo & M. A. S. D. Barros. 2015. "Effect of Solution pH on the Removal of Paracetamol by Activated Carbon of Dende Coconut Mesocarp". *Chemical and Biochemical Engineering*. Vol. 29, (1): p. 47–53.

Fei Company. 2003. "The Quanta FEG 200, 400, 600 User's Operation Manual". College of Engineering - UNL - University of Nebraska-Lincoln. <<http://engineering.unl.edu/downloads/files/UserManual-Quanta200SEM-sm.pdf>>. Accessed 30 September 2016.

Foo, K.Y. & B.H. Hameed. 2011. "Preparation and Characterization of Activated Carbon from Pistachio Nut Shells via Microwave-Induced Chemical Activation". *Biomass and Bioenergy*. Vol. 35, (7): p. 3257–3261.

Gad, H. M. H. & A. A. El-Sayed. 2009. "Activated Carbon from Agricultural By-products for the Removal Rhodamine-B from Aqueous Solution". *Journal of Hazardous Materials*. Vol. 168, (2-3): p. 1070-1081.

Ghosh, R. & S. Bhattacharjee. 2013. "A Review Study on Precipitated Silica and Activated Carbon from Rice Husk". *Chemical Engineering & Process Technology*. Vol. 4, (4): p. 1-7.

Ginsburg, N. 2016. "3 Key Differences of Bamboo, Coconut, & Hardwood Activated Charcoal". *Shopsagano*. <<http://www.shopsagano.com/blogs/news/115689348-3-key->

differences-of-bamboo-coconut-hardwood-activated-charcoal>. Accessed 19 April 2017.

Gisi, S. D., G. Lofrano, M. Grassi & M. Notarnicola. 2016. "Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review." *Sustainable Materials and Technologies* 9: 10-40. doi:<https://doi.org/10.1016/j.susmat.2016.06.002>.

Grima-Olmedo, C., A. Ramírez-Gómez, D. Gómez-Limón & C. Clemente-Jul. 2016. "Activated carbon from flash pyrolysis of eucalyptus residue." *Heliyon* 2 (9). doi:10.1016/j.heliyon.2016.e00155.

Grosman, A. & C. Ortega. 2008. "Capillary Condensation in Porous Materials: Hysteresis and Interaction without Pore Blocking/Percolation Process". *Langmuir*. Vol. 24, (8): p. A-J.

Guo, H. & X. L. Deng. 2013. "Preparation and Characterization of Activated Carbon from Palm Shell by Catalytic Activation with Steam". *Advanced Materials Research*. Vol. 787: p. 46-51.

Guo, S., J. Peng, W. Li, K. Yang, L. Zhang, S. Zhang & H. Xia. 2009. "Effects of CO₂ Activation on Porous Structures of Coconut Shell-Based Activated Carbons". *Applied Surface Science*. Vol. 255: p. 8443–8449.

Halbus, A. F., Z. H. Athab & F. H. Hussein. 2013. "Adsorption of Disperse Blue Dye on Iraqi Date Palm Seeds Activated Carbon". *International Journal of Chemical Science*. Vol. 11, (3): p. 1219-1233.

Hamdaoui, O. 2006. "Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick". *Journal of Hazardous Materials B*. Vol. 135: p. 264–273.

Hameed, B. H., J. M. Salman & A. L. Ahmad. 2009. "Adsorption Isotherm and Kinetic Modeling of 2,4-D Pesticide on Activated Carbon Derived from Date Stones". *Journal of Hazardous Materials*. Vol. 163: p. 121–126.

Hamza, U. D., N. S. Nasri, N. A. S. Amin, J. Mohammed & H. M. Zain. 2016. "Microwave assisted K₂CO₃ palm shell activated carbon as sorbent for CO₂ adsorption application." *Jurnal teknologi* 78 (8-3): 127–136. doi:10.11113/jt.v78.9576.

Hao, G. & D. Xianlun. 2013. "Preparation and characterisation of activated carbon from palm shell by catalytic activation with stream". *Advanced Materials Research*. Vol. 787: p. 46-51.

Hayashi, J., A. Kazehaya, K. Muroyama & A. P.I Watkinson. 2000. "Preparation of Activated Carbon from Lignin by Chemical Activation". *Carbon*. Vol. 38, (13): p. 1873–1878.

Hazza, R. A. 2014. "Phenol Adsorption from Simulated Wastewater on Rice Husk Activated Carbon and Granular Activated Carbon". Bull High Inst Public Health. Vol. 44, (2): p. 77-87.

Hidayat, A. & B. Sutrisno. 2017. "Comparison on Pore Development of Activated Carbon Produced by Chemical and Physical Activation from Palm Empty Fruit Bunch". Materials Science and Engineering. Vol. 162, (1): p. 1-8.

Higgins, F. & J. Seelenbinder. 2011. "Agilent Cary 630 Pharmacopoeia Compliance – Application Note". Agilent Technology. <<http://hpst.cz/sites/default/files/attachments/5990-9379en-appnote-630-pharma.pdf>>. Accessed 2 March 2016.

Ho, Y. S. & G. McKay. 1998. "A Comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents". Trans IChemE. Vol. 76, (Part B): p. 332-340.

Huang, P. H., H. H. Cheng, and S. H. Lin. 2015. "Adsorption of Carbon Dioxide onto Activated Carbon Prepared from Coconut Shells." Journal of Chemistry 2015: 1-10. doi:10.1155/2015/106590.

Huang, P. H., H. H. Cheng, & S. H. Lin. 2015. "Adsorption of Carbon Dioxide onto Activated Carbon Prepared from Coconut Shells." Journal of Chemistry 1-10. doi:10.1155/2015/106590.

Hui, T. S., & M. A. A. Zaini. 2015. "Potassium hydroxide activation of activated carbon: a commentary." Carbon Letters 16 (4): 275-280. doi:<http://dx.doi.org/10.5714/CL.2015.16.4.275>.

Hussaro, K. 2014. "Preparation of Activated Carbon from Palm Oil Shell by Chemical Activation with NaCO₃ and ZnCl₂ as Impregnated Agents for H₂S Adsorption". American Journal of Environmental Sciences. Vol. 10, (4): p. 336-346.

Illingworth, J., P. T. Williams & B. Rand. 2012. "Characterisation of biochar porosity from pyrolysis of biomass flax fibre." Journal of the Energy Institute 86 (2): 63-70. doi:10.1179/1743967112Z.000000000046.

Ilomuanya, M. O., B. Nashiru, N. D. Ifudu & C. I. Igwilo. 2016. "Effect of Pore Size and Morphology of Activated Charcoal Prepared from Midribs of *Elaeis guineensis* on Adsorption of Poisons using Metronidazole and *Escherichia coli* O157:H7 as a Case Study". Journal of Microscopy and Ultrastructure. Vol. 104: p. 1-7.

Ingole, R. S. & D. H. Lataye. 2015. "Adsorptive removal of phenol from aqueous solution using activated carbon prepared from babul sawdust". Journal of Hazardous, Toxic, and Radioactive Waste. Vol. 19, (4): p. 1-9.

Ioannidou, O. & A. Zabaniotou. 2007. "Agricultural Residues as Precursors for Activated Carbon Production—A Review". Renewable and Sustainable Energy Reviews. Vol. 11: p. 1966–2005.

Jain, A., R. Balasubramanian & M. P. Srinivasan. 2016. "Hydrothermal Conversion of Biomass Waste to Activated Carbon with High Porosity: A Review". Chemical engineering Journal. Vol. 283: p. 789-805.

Jodeh, S., F. Abdelwahab, N. Jaradat, I. Warad & W. Jodeh. 2016. "Adsorption of Diclofenac from Aqueous Solution using Cyclamen Persicum Tubers Based Activated Carbon (CTAC)". Journal of the Association of Arab Universities for Basic and Applied Sciences. Vol. 20: p. 32-38.

Jolliffe, I. T. & J. Cadima. 2016. "Principal Component Analysis: A Review and Recent Developments". Philos Trans A. Vol. 374(2065).

Kalavathy, M. H., T. Karthikeyan, S. Rajgopal & L. R. Miranda. 2005. "Kinetic and Isotherm Studies of Cu (II) Adsorption onto H₃PO₄-Activated Rubber Wood Sawdust". Journal of Colloid and Interface Science. Vol. 292, (2): p. 354–362.

Kalijadis, A. M., M. M. Vulcevic, Z. M. Jovanovic, Z. V. Lausevic & M. D. Lausevic. 2011. "Characterisation of surface oxygen groups on different carbon materials by the Boehm method and temperature-programmed desorption." Journal of Serbian Chemical Society 76 (5): 757–768. doi:10.2298/JSC091224056K.

Kamali, A. R. & D. J. Fray. 2013. "Molten salt corrosion of graphite as a possible way to make carbon nanostructures." Carbon 56: 121–131. doi:10.1016/j.carbon.2012.12.076.

Karagoz, S., T. Tay, S. Ucar & M. Erdem. 2008. "Activated Carbon from Waste Biomass by Sulfuric Acid Activation and Their Use on Methylene Blue Adsorption". Bioresource Technology. Vol. 99, (14): p. 6214-6222.

Kong, F. & R. P. Singh. 2008. "Disintegration of Solid Foods in Human Stomach." Journal of Food Science 73 (5): 67-80. doi:10.1111/j.1750-3841.2008.00766.x.

Khaled, A., A. El Nemr, A. El-Sikaily & O. Abdelwahab. 2009. "Removal of Direct N Blue-106 from Artificial Textile Dye Effluent Using Activated Carbon from Orange Peel: Adsorption Isotherm and Kinetic Studies". Vol. 165, (1-3): p. 100-110.

Kumar, A. & H. M. Jena. 2016. "Removal of methylene blue and phenol onto prepared activated carbon from Fox nutshell by chemical activation in batch and fixed-bed column". Journal of Cleaner Production. Vol. 137: p. 1246-1259.

Kumar, K. V. & K. Porkodi. 2007. "Mass Transfer, Kinetics and Equilibrium Studies for the Biosorption of Methylene Blue Using *Paspalum notatum*". Journal of Hazardous Materials. Vol. 146, (1-2): p. 214-226.

Kwaghger, A. & J. S. Ibrahim. 2013. "Optimization of Conditions for the Preparation of Activated Carbon from Mango Nuts using HCl". American Journal of Engineering Research. Vol. 2, (7): p. 74-85.

Langmuir, I. 1918. "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum". Journal of the American Chemical Society. Vol. 40, (9): p. 1361-1403.

Larous, S. & A. H. Meniai. 2016. "Adsorption of Diclofenac from Aqueous Solution Using Activated Carbon Prepared from Olive Stones". International Journal of Hydrogen Energy. Vol. 41, (24): p. 10380-10390.

Lee, M. S., M. Park, H. Y. Kim & S. J. Park. 2016. "Effects of Microporosity and Surface Chemistry on Separation Performances of N-Containing Pitch-Based Activated Carbons for CO₂/N₂ Binary Mixture." Scientific Report (23224). doi:10.1038/srep23224.

Li, B. 2012. "Characterization of Pore Structure and Surface Chemistry of Activated Carbons – A Review." In Fourier Transform - Materials Analysis, by S. Salih, 165-190. Rijeka: Intech. doi:10.5772/37460.

Li, K., Z. Zheng, X. Huang, G. Zhao, J. Feng & J. Zhang. 2009. "Equilibrium, Kinetic and Thermodynamic Studies on the Adsorption of 2-Nitroaniline onto Activated Carbon Prepared from Cotton Stalk Fiber". Journal of Hazardous Materials. Vol. 166, (1): p. 213-220.

Liu, Q. S., T. Zheng, P. Wang & L. Guo. 2010. "Preparation and Characterization of Activated Carbon from Bamboo by Microwave-Induced Phosphoric Acid Activation". Industrial Crops and Products. Vol. 31, (2): p. 233–238.

López, F.A., T.A. Centeno, O. Rodríguez & F.J. Alguacil. 2013. "Preparation and Characterization of Activated Carbon from the Char Produced in the Thermolysis of Granulated Scrap Tyres". Journal of the Air & Waste Management Association. Vol. 63, (5): p. 534-544.

Lukaszewicz, J. P. & K. Zichński. 2011. "Durability and Narrow Pore Size Distribution (PSD) of Carbons Fabricated from *Salix viminalis* Wood". Chemical and Process Engineering. Vol. 32, (3): p. 195-201.

Mak, S.M., B.T. Tey, K.Y. Cheah, W.L. Siew & K.K. Tan. 2009. "The effect of mechanical grinding on the mesoporosity of steam-activated palmkernel shell activated carbons". Journal of Chemical Technology and Biotechnology. Vol. 84: p. 1405–1411.

Manocha, S. M. 2003. "Porous Carbons". Sadhana. Vol. 28, (1-2): p. 335–348.

Marsh, H. & F. R. Reinoso. 2006. *Characterization of Activated Carbon*. Activated Carbon, by Harry Marsh and Francisco Rodríguez Reinoso, 143-242. Oxford: Elsevier Ltd.

Matricardi, M. & A. P. McNally. 2014. "The direct assimilation of principal components of IASI spectra in the ECMWF 4D-Var." Quarterly Journal of the Royal Meteorological Society 140: 573–582. doi:10.1002/qj.2156.

Mazlan, M. A. F., Y. Uemura, N. B. Osman & S. Yusup . 2015. "Characterizations of Bio-char from Fast Pyrolysis of Meranti Wood Sawdust." *Journal of Physics: Conference Series* 622: 1-7. doi:10.1088/1742-6596/622/1/012054.

MCB (Malaysian Cocoa Board). 2016. "Statistics - Cocoa Cultivated Area by Region and Sector (ha)". *Malaysian Cocoa Board*. <<http://www.koko.gov.my/lkm/industry/statistic/cocoacultivated.cfm>>. Accessed 12 August 2017.

Micromeritics. 2011. "ASAP 2020 Accelerated Surface Area and Porosimetry System - Operator's Manual". Iowa State University. October. http://www.cif.iastate.edu/sites/default/files/uploads/Other_Inst/BEI/ASAP2020%20Operator's%20Manual.pdf.

MOH - Ministry of Health. 2016. "Food Regulation 1985". In *Food Act 1983*, by Law of Malaysia, 32. Petaling Jaya, Selangor: International Law Book Services.

Mohd Din, A. T., B. H. Hameed & A. L. Ahmad. 2009. "Batch Adsorption of Phenol onto Physiochemical-Activated Coconut Shell". *Journal of Hazardous Materials*. Vol. 161, (2-3): p. 1522-1529.

Mopoung, S. 2008. "Surface Image of Charcoal and Activated Charcoal from Banana Peel". *Journal of Microscopy Society of Thailand*. Vol. 22: p. 15-19.

Mylsamy, S. & C. Theivarasu. 2012. "Adsorption of Reactive Dye Using Low Cost Adsorbent: Cocoa (*Theobroma Cacao*) Shell". *World Journal of Applied Environmental Chemistry*. Vol. 1, (1): p. 22-29.

Nakagawa, Y., M. Molina-Sabio & P. Rodríguez-Reinoso. 2007. "Modification of the porous structure along the preparation of activated carbon monoliths with H_3PO_4 and $ZnCl_2$ ". *Microporous and Mesoporous Materials*. Vol. 103: p. 29-34.

NCBI. 2017. "Salicylate". National Center for Biotechnology Information. <https://pubchem.ncbi.nlm.nih.gov/compound/salicylate#section=Top>.

Nfor, B. K., O. T. Forton, T. A. Benu & P. D. E. M. Verhaert. 2012. "Valorization of by-products of cocoa production - towards a more sustainable cocoa value chain in Cameroon". *foundation-imagine.org*. <http://www.foundation-imagine.org/uploads/media/Valorization_of_cocoa_byproducts_in_Cameroon.pdf>. Accessed 12 August 2016.

Ng, K. C., M. Burhan, M. W. Shahzad & A. Ismail. 2017. "A Universal Isotherm Model to Capture Adsorption Uptake and Energy Distribution of Porous Heterogeneous Surface." *Scientific Reports* 7 (10634). doi:<https://doi.org/10.1038/s41598-017-11156-6>.

Nguyen, L. N., F. I. Hai, J. Kang, W. E. Prince & L. D. Nghiem. 2013. "Coupling Granular Activated Carbon Adsorption with Membrane Bioreactor Treatment for Trace

Organic Contaminant Removal: Breakthrough Behavior of Persistent and Hydrophilic Compounds". *Journal of Environmental Management*. Vol. 119: p. 173-181.

Nikman, K. A. 2017. "Cocoa's own private collection". Nilai, Negeri Sembilan. Photographed 20 February 2017.

Nimmo, J. R. 2004. "Porosity and Pore Size Distribution". In *Encyclopedia of Soils in the Environment*, by D. Hillel, 295-303. London: Elsevier.

Njoku, V.O. & B.H. Hameed. 2011. "Preparation and Characterization of Activated Carbon from Corncob by Chemical Activation with H_3PO_4 for 2, 4-dichlorophenoxyacetic Acid Adsorption". *Chemical Engineering Journal*. Vol. 173, (2): p. 391-399.

Norzilah, A. H., A. Fakhru'l-Razi, T. S. Y. Choong & A. L. Chuan. 2011. "Surface Modification Effects on CNTs Adsorption of Methylene Blue and Phenol". *Journal of Nanomaterials*. Vol. 2011: p. 1-18.

Nowicki, P., J. Kazmierczak & R. Pietrzak. 2015. "Comparison of Physicochemical and Sorption Properties of Activated Carbons Prepared by Physical and Chemical Activation of Cherry Stones." *Powder Technology* 269: 312-319. doi:<https://doi.org/10.1016/j.powtec.2014.09.023>.

Nsami, J. N. & J. K. Mbadcam. 2013. "The Adsorption Efficiency of Chemically Prepared Activated Carbon from Cola Nut Shells by $ZnCl_2$ on Methylene Blue" *Journal of Chemistry*. Vol. 2013: p. 1-7.

Nuithitikul, K., S. Srikhun & S. Hirunpraditkoon. 2010. "Influences of Pyrolysis Condition and Acid Treatment on Properties of Durian Peel-Based Activated Carbon". *Bioresource Technology*. Vol. 101, (1): p. 426-429.

Okewale, A. O., P. K. Igbokwe & O. A. Adesina. 2015. "Optimization of the Adsorptive Dehydration of Ethanol - Water System". *Chemical and Process Engineering Research*. Vol.39: p. 27-37.

Okman, I., S. Karagöz, T. Tay & M. Erdem. 2014. "Activated Carbons from Grape Seeds by Chemical Activation with Potassium Carbonate and Potassium Hydroxide". *Applied Surface Science*. Vol. 293: p. 138- 142.

Onianwa, P.C., I.G. Adetola, C.M.A. Iwegbue, M.F. Ojo & O.O. Tella. 1999. "Trace heavy metals composition of some Nigerian beverages and food drinks". *Food Chemistry*. Vol. 66: p. 275-279.

Opara, C. C., A. I. Oyom & M. C. Okonkwo. 2013. "Deodorization of Kerosene Using Activated Carbon as Adsorbent". *Greener Journal of Physical Sciences*. Vol. 3, (2): p. 70-75.

- Orkun, Y., N. Karatepe & R. Yavuz. 2012. "Influence of Temperature and Impregnation Ratio of H₃PO₄ Influence of Temperature and Impregnation Ratio of H₃PO₄" *Acta Physica Polonica A*. Vol. 121: p. 277-280.
- Palanichamy, K., K. Ariharaputhiran & A. Darchen. 2013. "Activated Carbon from Grass – A Green Alternative Catalyst Support for Water Electrolysis". *International Journal of Hydrogen Energy*. Vol. 38, (25): p. 10364-10372.
- Panchalingam, K., M. Noh, Y. H. Huh & J. L. Sherley . 2016. "Distributed Stem Cell Kinetotoxicity: A New Concept to Account for the Human Carcinogenicity of Non-genotoxic Environmental Toxicants." Chap. 10 in *Human Stem Cell Toxicology*, by J. L. Sherley, 250-279. Cambridge: The Royal Society of Chemistry.
- Pathak, P. D., S. A. & B. D. Kulkarni. 2015. "Utilization of banana peel for the removal of benzoic and salicylic acid from aqueous solutions and its potential reuse". *Desalination and Water Treatment*. Vol. 2015: p. 1-13.
- Pathan, A. K., J. Bond & R. E. Gaskin. 2010. "Sample preparation for SEM of plant surfaces." *Materials Today* 12 (1): 32-43. doi:[https://doi.org/10.1016/S1369-7021\(10\)70143-7](https://doi.org/10.1016/S1369-7021(10)70143-7).
- Prahas, D., Y. Kartika, N. Indraswati & S. Ismadji. 2008. "Activated Carbon from Jackfruit Peel Waste by H₃PO₄ Chemical Activation: Pore Structure and Surface Chemistry Characterization". *Chemical Engineering Journal*. Vol. 140, (1): p. 32-42.
- Pua, F. L., M. S. Sajab, C. H. Chia, S. Zakaria, I. A. Rahman & M. S. Salit. 2013. "Alkaline-treated cocoa pod husk as adsorbent for removing methylene blue from aqueous solutions". *Journal of Environmental Chemical Engineering*. Vol. 1: p. 460–465.
- Purnomo, C. W., C. Salim & H. Hinode. 2012. "Synthesis of Pure Na-X and Na-A Zeolite from Bagasse Fly Ash". *Microporous and Mesoporous Materials*. Vol. 162: p. 6-13.
- Rafiq, M. K., R. T. Bachmann, M. T. Rafiq, Z. Shang & S. Joseph. 2016. "Influence of Pyrolysis Temperature on Physico-Chemical Properties of Corn Stover (*Zea mays* L.) Biochar and Feasibility for Carbon Capture and Energy Balance". *Plos One*. Vol. 11, (6): p. 1-17.
- Rankin, C. W., J. O. Nriagu, J. K. Aggarwal, T. A. Arowolo, K. Adebayo & A. R. Flegal. 2005. "Lead Contamination in Cocoa and Cocoa Products: Isotopic Evidence of Global Contamination". *Environment Health Perspectives*. Vol. 113 (10): 1344–1348.
- Rao, V. V. B. & S. R. M. Rao. 2006. "Adsorption Studies on Treatment of Textile Dyeing Industrial Effluent by Flyash". *Chemical Engineering Journal*. Vol. 116: p. 77–84.
- Raoul, T. T. D., A. S. Gabche, N. G. Ndifor-A & K. J. Mbadcam. 2015. "Adsorption of Salicylic and Sulfosalicylic Acid onto Powdered Activated Carbon prepared from Rice

and Coffee Husks". International Journal of Current Engineering and Technology. Vol. 5, (3): p. 1641-1652.

Rashidi, N. A., S. Yusup & A. Borhan. 2014. "Development of Novel Low-Cost Activated Carbon for Carbon Dioxide Capture". International Journal of Chemical Engineering and Applications. Vol. 5, (2): p. 90-94.

Reay, D. 2013. "Glycerin Purification with Activated Carbon". *chemvironcarbon*.. <www.chemvironcarbon.com>. Accessed 8 May 2017.

Ribas, M. C., M. A. Adebayo, L. D.T. Prola, E. C. Lima, R. Cataluña, L. A. Feris, M.J. Puchana-Rosero, F. M. Machado, F. A. Pavan & T. Calvete. 2014. "Comparison of a Homemade Cocoa Shell Activated Carbon with Commercial Activated Carbon for the Removal of Reactive Violet 5 Dye from Aqueous Solutions". Chemical Engineering Journal. Vol. 248: p. 315-326.

Roberts, J. R., E. J. Gracely & J. M. Schoffstall. 1997. "Advantage of High-Surface-Area Charcoal for Gastrointestinal Decontamination in a Human Acetaminophen Ingestion Model". Academic Emergency Medicine. Vol. 4: p. 167-174.

Rodriguez-Reinoso, F. & M. Molina-Sabio. 1992. "Activated Carbons from Lignocellulosic Materials by Chemical and/or Physical Activation. An Overview". Carbon. Vol. 30, (7): p. 1111-1118.

Rozhan, A. N. & H. Purwanto. 2015. "Development Process for Tar Filtering from Biomass Pyrolysis". WIT Transactions on Ecology and the Environment. Vol. 206: p. 315-323.

Ruíz-Baltazar, A. & R. Perez. 2015. "Kinetic Adsorption Study of Silver Nanoparticles on Natural Zeolite: Experimental and Theoretical Models." Applied Sciences 5: 1869-1881. doi:10.3390/app5041869.

Sahira, J., A. Mandira, P. B. Prasad & P. R. Ram. 2013. "Effects of Activating Agents on the Activated Carbons Prepared from Lapsi Seed Stone". Research Journal of Chemical Sciences. Vol. 3, (5): p. 19-24.

Saini, M. K., P. K. Srivastava & N. Choudhury. 2015. "Development of Moisture and Ash Based Correlation for the Estimation of Mineral Matter in High Ash Indian Coal" International Journal of Clean Coal and Energy. Vol. 4: p. 33-42.

Salleh, N. A. M. & M. S. Hassan. 2015. "Principal Component Analysis (PCA) on Multivariate Data of Lard Analysis in Cooking Oil". Journal of Mathematics and System Science. Vol. 5: p. 300-306.

Salman, J. M. & B. H. Hameed. 2010. "Effect of Preparation Conditions of Oil Palm Fronds Activated Carbon on Adsorption of Bentazon from Aqueous Solutions". Journal of Hazardous Materials. Vol. 175, (1-3): p. 133-137.

Saucier, C., M. A. Adebayo, E. C. Lima, R. Cataluña, P. S. Thue, L. D.T. Prola, M.J. Puchana-Rosero, F. M. Machado, F. A. Pavan & G.L. Dotto. 2015. "Microwave-Assisted Activated Carbon from Cocoa Shell as Adsorbent for Removal of Sodium Diclofenac and Nimesulide from Aqueous Effluents". *Journal of Hazardous Materials*. Vol. 289: p. 18–27.

Schröder, E. & K. Thomauske, B. Oechsler, S. Herberger, S. Baur & A. Hornung. 2011. *Activated Carbon from Waste Biomass. Progress in Biomass and Bioenergy Production*. p. 333-356. In book: *Progress in Biomass and Bioenergy Production*, Chapter: *Activated Carbon from Waste Biomass*, Publisher: InTech

Sebbahi, S., A. Ahmido, F. Kifani-Sahban, S. E. Hajjaji & A. Zoulalian. 2014. "Preoxidation and Activation of the Lignin Char: Carbonization and Oxidation Procedures". *Journal of Engineering*. p. 1-9.

Sentorun-Shalaby, C., M. G. Uçak-Astarlıoğlu, L. Arıok & Ç. Sarıcı. 2006. "Preparation and Characterization of Activated Carbons by One-Step Steam Pyrolysis/Activation from Apricot Stones". *Microporous and Mesoporous Materials*. Vol. 88: p. 126-134.

Shahmohammadi-Kalalagh, Sh., H. Babazadeh, A. H. Nazemi & M. Manshouri. 2011. "Isotherm and Kinetic Studies on Adsorption of Pb, Zn and Cu by Kaolinite". *Caspian Journal of Environmental Sciences*. Vol. 9, (2): p. 243-255.

Shawabkeh, R. A., Z. Aslam & I. A. Hussien. 2015. "Thermochemical Treatment of Fly Ash for Synthesis of Mesoporous Activated Carbon". *Journal of Thermal Analysis and Calorimetry*. Vol. 122: p. 1-12.

Singleton, 2015. "Why Is Phosphoric Acid Bad for You? *Livestrong*. <<http://www.livestrong.com/article/468217-why-is-phosphoric-acid-bad-for-you/>>. Accessed August 1, 2017.

Srihari, V. & A. Das. 2008. "The Kinetic and Thermodynamic Studies of Phenol-Sorption onto Three Agro-Based Carbons". *Desalination*. Vol. 225: p. 220-234.

Suhas, P.J.M. Carrott & M.M.L. Ribeiro Carrott. 2007. "Lignin – from Natural Adsorbent to Activated Carbon: A review". *Bioresource Technology*. Vol. 98, (12): p. 2301–2312.

Sun, L. B., Y. H. Kang, Y. Q. Shi, Y. Jiang & X. Q. Liu. 2015. "Highly Selective Capture of the Greenhouse Gas CO₂ in Polymers". *ACS Sustainable Chemistry Engineering*. Vol. 3: p. 3077-3085.

Swiderska-Dabrowska, R. & R. Schmidt. 2013. "Adsorption of phenol on clinoptilolite modified by cobaltions". In *Environmental Engineering IV*, edited by Artur Pawlowski, Marzenna R. Dudzinska and Lucjan Pawlowski, 97-101. London: CRC Press - Taylor & Francis Group.

Tan, I. A. W., A. L. Ahmad & B. H. Hameed. 2008. "Adsorption of Basic Dye on High-Surface-Area Activated Carbon Prepared from Coconut Husk: Equilibrium, kinetic and thermodynamic studies". *Journal of Hazardous Materials*. Vol. 154, (1-3): p. 337-346.

Tan, I. A. W., A. L. Ahmad & B. H. Hameed. 2009. "Adsorption Isotherms, Kinetics, Thermodynamics and Desorption Studies of 2, 4, 6-trichlorophenol on Oil Palm Empty Fruit Bunch-Based Activated Carbon". *Journal of Hazardous Materials*. Vol. 164, (2-3): p. 473-482.

Tay, T., S. Ucar & S. Karagoz. 2009. "Preparation and Characterization of Activated Carbon from Waste Biomass". *Journal of Hazardous Materials*. Vol. 165, (1-3): p. 481-485.

Tchapda, A. H. & S. V. Pisupati. 2014. "A Review of Thermal Co-Conversion of Coal and Biomass/Waste". *Energies*. Vol. 7: p. 1098-1148.

Temdrara, L., A. Addoun & A. Khelifi. 2015. "Development of Olivestones-Activated Carbons by Physical, Chemical and Physicochemical Methods for Phenol Removal: A Comparative Study." *Desalination and Water Treatment* 53 (2): 452-461. doi:<https://doi.org/10.1080/19443994.2013.838523>.

Theivarasu, C. & S. Mylsamy. 2010. "Equilibrium and Kinetic Adsorption Studies of Rhodamine-B from Aqueous Solutions Using Cocoa Shell as a New Adsorbent". *International Journal of Engineering Science and Technology*, Vol. 2, (11): p. 6284-6292.

Theivarasu, C. & S. Mylsamy. 2011. "Removal of Malachite Green from Aqueous Solution by Activated Carbon Developed from Cocoa (*Theobroma Cacao*) Shell - A Kinetic and Equilibrium Studies". *E-Journal of Chemistry*, Vol. 8, (1): p. 363-371.

Thiruvelan. 2014. Digestion pH. August 4. Accessed June 25, 2018. <http://gastrodigestivesystem.com/digestion/digestion-ph>.

Thommes, M., K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol & K. S.W. Sing. 2015. "Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report)". *Pure and Applied Chemistry* p. 1-19.

Tongpoothorn, W., M. Sriuttha, P. Homchan, S. Chanthai & C. Ruangviriyachai. 2011. "Preparation of Activated Carbon Derived from *Jatropha curcas* Fruit Shell by Simple Thermo-Chemical Activation and Characterization of Their Physico-Chemical Properties". *Chemical Engineering Research and Design*. Vol. 89, (3): p. 335-340.

Vadivelan, V. & K. V. Kumar. 2005. "Equilibrium, Kinetics, Mechanism, and Process Design for the Sorption of Methylene Blue onto Rice Husk". *Journal of Colloid and Interface Science*. Vol. 286, (1): p. 90-100.

van Vliet, J. A., M. Slingerland & K. E. Giller. 2015. Mineral Nutrition of Cocoa: A Review. Review, Wageningen: Wageningen University and Research Centre.

Veksha, A., T. I. Bhuiyan & J. M. Hill. 2016. "Activation of Aspen Wood with Carbon Dioxide and Phosphoric Acid for Removal of Total Organic Carbon from Oil Sands Produced Water: Increasing the Yield with Bio-Oil Recycling." *Materials* 9 (20): 1-13. doi:10.3390/ma9010020.

Wang, L., Ø. Skreiberg, S. V. Wesenbeeck, M. G. Gronli & M. J. Antal. 2016. "Experimental Study on Charcoal Production from Woody Biomass". *Energy & Fuels*. p. 1-43.

Wu, M., D. Atchley, L. Greer, S. Janssen, D. Rosenberg & J. Sass. 2009. *Dosed Without Prescription: Preventing Pharmaceutical. White Paper*, NRDC.

Wu, M., Q. Guo & G. Fu. 2013. "Preparation and Characteristics of Medicinal Activated Carbon Powders by CO₂ Activation of Peanut Shells". *Powder Technology*. Vol. 247 : p. 188–196.

Wuana, R. A. & F. E. Okieimen. 2011. "Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation" *International Scholarly Research Network Ecology*. Vol. 2011: p. 1-20.

XAmplified. 2009. Adsorption Isotherm. March 6. Accessed June 22, 2018. <http://www.chemistrylearning.com/adsorption-isotherm/>.

Yahya, M. A., Z. Al-Qodah & C.W. Z. Ngah. 2015. "Agricultural Bio-Waste Materials as Potential Sustainable Precursors used for Activated Carbon Production: A Review". *Renewable and Sustainable Energy Reviews*. Vol. 46: p. 218–235.

Yakout, S.M. & G. S. El-Deen. 2016. "Characterization of Activated Carbon Prepared by Phosphoric Acid Activation of Olive Stones". *Arabian Journal of Chemistry*. Vol. 9, (S2): p. 1155–1162.

Yang, R. T. 2003. "Activated Carbon." In *Adsorbents: Fundamentals and Applications*, by Ralph T. Yang, 79-130. New Jersey: John Wiley & Sons, Inc.

Yener, J., T. Kopac, G. Dogu & T. Dogu. 2008. "Dynamic Analysis of Sorption of Methylene Blue Dye on Granular and Powdered Activated Carbon". *Chemical Engineering Journal*. Vol. 144, (3): p. 400-406.

Zafar, S. 2015. "Agricultural Biomass in Malaysia". *BioEnergy Consult*. <<https://www.bioenergyconsult.com/agricultural-biomass-in-malaysia/>>. Accessed 6 November 2017.

Zhao, W., L. Luo, H. Wang & M. Fan. 2017. "Synthesis of Bamboo-Based Activated Carbons with Super-High Specific Surface Area for Hydrogen Storage". *BioResources*. Vol. 12, (1): p. 1246-1262.

Zhang, T., W. P. Walawender, L. T. Fan, M. Fan, D. Daugaard & R.C. Brown. 2004. "Preparation of Activated Carbon from Forest and Agricultural Residues through CO₂ Activation". Chemical Engineering Journals. Vol. 105, (1-2): p. 53–59.

Zhang, S., L. Tao, Y. Zhang, Z. Wang, G. Gou, M. Jiang, C. Huang & Z. Zhou. 2016. "The role and mechanism of K₂CO₃ and Fe₃O₄ in the preparation of magnetic peanut shell based activated carbon". Powder Technology. Vol. 295: p. 152-160.

Zhao, S. X., N. Ta & X. D. Wang . 2017. "Effect of Temperature on the Structural and Physicochemical Properties of Biochar with Apple Tree Branches as Feedstock Material." Energies 10 (1293): 1-15. doi:10.3390/en10091293.

Zhou, Y. & R. M. Raphael. 2005. "Effect of salicylate on the elasticity, bending stiffness, and strength of SOPC membranes". Biophysical Journal. Vol. 89, (3): p. 1789-801.

CONFERENCE/SEMINAR/EXHIBITION

1. Nikman, K. A., F. Ahmad, M. S. Hassan & M. A. Ahmad. 2016. Substances Intoxication – An instant remedy from cocoa. 11th Allied Health Scientific Conference Malaysia 2016. Bahagian Sains Kesihatan Bersekutu, Kementerian Kesihatan Malaysia. Mahkota Ballroom, Ballroom Level, Hotel Istana, Kuala Lumpur. **Poster.**
2. Nikman, K. A., F. Ahmad, M. S. Hassan, M. A. Ahmad & K. Nikman. 2016. The effects of chemical activation, on porosity and surface functional groups of cocoa (*Theobroma cacao*) nib-based activated carbon. Malaysian Cocoa Board Scientist Workshop 2016. Malaysian Cocoa Board. Institut Semarak Felda (ISEF), Bangi Government and Private Training Centre Area, Selangor. **Oral.**
3. Nikman, K. A., F. Ahmad, M. S. Hassan & M. A. Ahmad. 2016. The adsorption capacity of chemically prepared activated carbon from cocoa (*Theobroma cacao*) nibs on methylene blue. National Conference on the Science and Social Science 2016. Open University Malaysia, Negeri Sembilan Learning Centre, Seremban, Negeri Sembilan. **Oral.**
4. Nikman, K. A., F. Ahmad, M. S. Hassan, M. A. Ahmad & K. Nikman. 2016. The effects of chemical activation, on porosity and surface functional groups of cocoa (*Theobroma cacao*) nib-based activated carbon. Seoul International Invention Fair (SIIF 2016). COEX Convention and Exhibition Center, Seoul, South Korea. **Poster.**

AWARD

Bronze Medal. Seoul International Invention Fair (SIIF 2016). COEX Convention and Exhibition Center, Seoul, South Korea.

PUBLICATION

1. Nikman, K. A., F. Ahmad, M. S. Hassan, M. A. Ahmad & Nikman, K. 2017. Adsorption of Chemically Prepared Cocoa Nibs Based Activated Carbon Onto Methylene Blue: Equilibrium and Kinetic Studies. International Journal of Petrochemistry and Research. Vol. 1(1): p. 15-18.
2. Nikman, K. A., F. Ahmad & M. S. Hassan. 2018. Removal of methylene blue from aqueous solution using cocoa (*Theobroma cacao*) nib-based activated carbon treated with hydrochloric acid. Malaysian Journal of Fundamental and Applied Sciences. Vol. 14(2): p. 193-197.

Adsorption of Chemically Prepared Cocoa Nibs Based Activated Carbon Onto Methylene Blue: Equilibrium and Kinetic Studies

KhairulAdli N^{1,2}, Faisal A³, MohdSukri H¹, Khairunisa N⁴ and Ahmad MA^{5,6*}

¹Faculty of Science and Technology, Universiti Sains Islam Malaysia, 71800 Nilai, Negeri Sembilan, Malaysia.

²Jabatan Perubatan Forensik, Hospital Kuala Lumpur, 50586 Kuala Lumpur, Malaysia

³Cocoa Innovative and Technology Centre, Malaysian Cocoa Board, Lot 12621, 71800 Nilai, Negeri Sembilan, Malaysia.

⁴Academy of Language Studies, Universiti Teknologi MARA Pahang, Bandar Tun Abdul Razak, Jengka, Pahang, Malaysia.

⁵School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 11300 Nibong Tebal, Penang, Malaysia.

⁶Solid Waste Management Cluster, Science & Engineering Research Centre, Engineering Campus, Universiti Sains Malaysia, Nibong Tebal, Penang, Malaysia.

Article Info

*Corresponding author:

Mohd Azmier Ahmad

Associate Professor

School of Chemical Engineering

Engineering Campus

Universiti Sains Malaysia

14300 Nibong Tebal, Penang, Malaysia

Tel. +604 5996459

Fax: +604 5996908

E-mail: chazmier@usm.my

doi: 10.18689/ijpr.2017-104

Received: March 23, 2017

Accepted: April 4, 2017

Published: April 10, 2017

Citation: KhairulAdli N, Faisal A, MohdSukri H, Khairunisa N and Ahmad MA*. Adsorption of Chemically Prepared Cocoa Nibs Based Activated Carbon Onto Methylene Blue: Equilibrium and Kinetic Studies. *Int J Pet Res*. 2017; 1(1): 15-18.

Copyright: © 2017 Ahmad MA et al. This work is licensed under a Creative Commons Attribution 4.0 International license, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Published by Madridge Publishers

Abstract

This study was aimed to prepare cocoa nibs based activated carbon (CNAC) via chemical activation for methylene blue (MB) dye adsorption from aqueous solution. The activation process was performed at 500°C under inert condition using K_2CO_3 as activation agent. The effect of contact time and initial concentration of adsorbate on the adsorption process were examined. Langmuir isotherm model fitted well the adsorption equilibrium data with monolayer adsorption capacity of 64.98 mg/g at 30°C. The adsorption kinetic was found to follow the pseudo-second-order kinetic model.

Keywords: Activated carbon, Chemical activation, Cocoa nibs, Methylene blue.

Introduction

Water pollution has become a highlighted issue as some of the industrial effluent is directly discharged into the river and water bodies without proper treatment [1]. Dyes effluent treatments from textile industries are divided into biological, physical and chemical treatment processes. All these processes have different color removal capabilities, capital costs and operating rates [2]. Physical treatment via adsorption process using Agrowaste based activated carbon as adsorbent is among the most efficient and cheap method for dyes removal. Several studies on agrowastes have been employed to remove the contaminants such as methylene blue (MB) dye from the water bodies [3] [4]. Agrowaste is appreciated as economical, sustainable and ecologically friendly materials. In this study, an attempt was made to utilize cocoa nibs waste into activated carbon using chemical activation process. The performance of CNAC was studied in removing MB dye from aqueous solution.

Experimental

Chemicals

All reagents and chemicals used in the research were analytical grade chemicals. For impregnation process, potassium carbonate (K_2CO_3) was used. Commercial methylene blue ($C_{16}H_{18}ClN_3S \cdot 3H_2O$) (MB) textile dye was obtained from Sigma-Aldrich (M) Sdn Bhd.

Preparation of Stock and Test Solutions

Stock solution of MB with concentration of 500 mg/L was prepared by dissolving approximately 0.50 g of MB in 1000 mL distilled water. Test solution of MB ranging from 10 mg/L to 100 mg/L were prepared by subsequent dilution from stock solution.

Production of Pellet

The cocoa nibs waste was ground and sifted to a uniform size of 0.5 mm or smaller. The samples were shaped into pellets by compressing the mixture with a hydraulic press, in which the cocoa nibs were compacted into pellets with a specific density of 1.8 g/cm.

Preparation of Activated Carbon

The carbonization was performed by placing approximately 60 g of cocoa nibs pellet in a vertical furnace, which contained in a tubular stainless steel reactor. This step was carried out at 700°C for 1 hour under purified nitrogen (99.99%) with flowrate of 120 mL/min. Then, the furnace was allowed to cold to ambient temperature. Char yield was determined using following equation:

$$\% \text{ Yield} = \frac{w_c}{w_i} \times 100\% \quad (1)$$

where w_c is the mass of char after carbonization process and w_i is the initial mass of cocoa nibs pellet. An amount of dried char was added with K_2CO_3 at various impregnation ratio (IR) in a 250 ml beaker. Both were mixed with deionized water to dissolve the salt. The IR was calculated as follows:

$$\text{Impregnation ratio, IR} = \frac{w_{K_2CO_3}}{w_{\text{char}}} \quad (2)$$

where $w_{K_2CO_3}$ is the dry weight of potassium carbonate pellets and w_{char} is the dry weight of cocoa nibs char. The mixture was then dehydrated in an oven at 105°C for 24 hours. The activation step was done using similar reactor as in carbonization step but at final temperature of 500°C under nitrogen flowrate of 120 mL/min for 2 hours. The sample was then cooled to room temperature and washed with hot deionized water until the pH of the washed solution reached 6.5-7.

Removal of MB by Batch Adsorption Study

The batch equilibrium experiments of the adsorption capacity studies were conducted at 30 °C in a 250 mL conical flask in a water bath shaker. The stock solution (1000 mg/L) of MB was prepared by dissolving approximately weighed 1.0 gram of the MB in 1000 mL of distilled water in a 1500 mL volumetric flask. The stock solutions were stored in dark place to prevent direct sunlight. The sample solutions were withdrawn at equilibrium to determine the residual concentration. The concentrations of the filtrates were measured using UV-Visible Spectrophotometer (Model Agilent Cary 60, USA).

Effect of Initial Concentration

In order to study the effects of initial adsorbate concentration, 100 mL of adsorbate solutions with known initial concentration (10, 25, 50, 80, 100 mg/L of MB) were prepared in a series of 250 mL Erlenmeyer flasks. The amount of adsorbent that was added into each flask was fixed at 0.1 g. The flasks were placed

in an isothermal water bath shaker at temperature and rotation speed of 30°C and 120 rpm, respectively until equilibrium point was reached.

Effect of Contact Time

In order to study the effects of contact time on the adsorption uptake, 100 mL of adsorbate solutions with known initial concentration (10-100 mg/L) were prepared in a series of 250 mL Erlenmeyer flasks. The amount of CNAC that was added into each flask containing MB solution was fixed at 0.1 g. The flasks were then placed in an isothermal water bath shaker of 30 °C with rotation speed of 120 rpm for 360 minutes. The percent removal of adsorbate was calculated as follows:

$$\% \text{ Removal} = \frac{(C_i - C_e)}{C_i} \times 100\% \quad (3)$$

Where C_e is the concentration of adsorbate at equilibrium and C_i is the initial concentration of adsorbate. The MB uptake at equilibrium is calculated as follows:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (4)$$

where m is the mass of the adsorbent and V is the volume of the adsorbate.

Adsorption Isotherm

Adsorption isotherm study was carried out by fitting the equilibrium data to three isotherm model which are the Langmuir and Freundlich isotherm models, respectively represented by Equations (5), (6) and (7). The applicability and suitability of the isotherm equation to the equilibrium data was compared by judging the values of the correlation coefficients, R^2 . The Langmuir model is atypical model used to measure the amount of adsorbate on an adsorbent at equilibrium. The relation is expressed by following equation [5]:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (5)$$

where, q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the metal ion (mg/L), q_m is the maximum amount of adsorbed metal ion per unit mass of sorbent corresponding to complete coverage of the adsorptive sites (mg/g), K_L is the Langmuir constant related to the energy of adsorption (L/mg)

The Freundlich adsorption isotherm or Freundlich equations are a relation between the concentrations of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. The relationship is stated as follows [6]:

$$q_e = k_f C_e^{\frac{1}{n}} \quad (6)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (7)$$

In this equation, q_e (mg/g) is amount of adsorbed material in adsorbent surface k in arrangement are adsorption capacity and adsorption intensification.

Kinetic Model

The kinetics of adsorption describes the rate of adsorbate uptake on activated carbon prepared and it controls the equilibrium time. The kinetics of adsorbate uptake is required for selecting optimum operating conditions for the full-scale batch process. Therefore, models for liquid-phase adsorption such as pseudo-first-order and pseudo-second-order were used to analyze the adsorption kinetic data. The pseudo-first-order kinetic model equation of Lagergren [7] is generally expressed as:

ln(q_e - q_t) = lnq_e - k₁ t (8)

Where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), q_t is the amount of solute adsorb per unit weight of adsorbent at time (mg/g), k₁ is the rate constant of pseudo-first order sorption (1/h). The pseudo-second-order equation is expressed as [8]:

t/q_t = t/(k₂ q_e²) + t/q_e (9)

Where k₂ is the rate constant of pseudo-second-order sorption (g/h.mg).

Results and Discussion

Effect of contact time and MB initial concentration on adsorption equilibrium

Figure 2 and Table 1 show the effect of various initial concentrations on adsorption of MB by CNAC. An equilibrium time of 100 min was needed for MB dye solution with initial concentrations of 10-25 mg/l to reach equilibrium. However, for initial concentrations of 50-100 mg/l, longer equilibrium times of 22-24 hours were required for the system to reach equilibrium. Initially, adsorbate molecules have to first encounter the boundary layer effect. Then it has to diffuse from boundary layer film onto adsorbent surface and finally, it has to diffuse into the porous structure of the adsorbent [10]. The ratio of the initial number of dye molecules to the available surface area was low at lower initial concentration compared to higher initial concentration. Therefore, MB solution with higher initial concentration would take relatively longer contact time to attain equilibrium due to the higher amount of MB molecules.

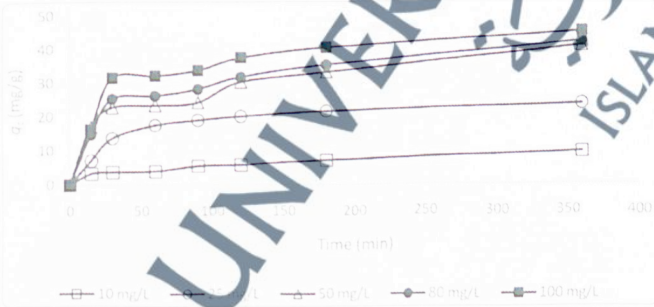


Fig. 2: Effects of contact time of MB onto CNAC

Table 1. MB percent removal by CNAC with IR 3:1

Initial Concentration (mg/L)	Concentration Left (mg/L)	Concentration Adsorbed (mg/L)	Percent Removal (%)	Concentration adsorbed at equilibrium, q _e (mg/g)
10	0.00	10.00	100.0	5.00
25	5.04	19.96	79.8	9.98
50	11.57	38.43	76.9	19.22
80	25.16	54.84	68.6	27.42
100	33.39	66.61	66.6	33.31

Effect of IR on adsorption equilibrium

Fig. 1 shows the influence of IR on CNAC in removing MB. Sample impregnated with 2:1 ratio has the lowest capability to adsorb the adsorbate where the value is 27.8 mg/g.



Fig. 1: Effect of IR on MB uptake

The adsorption capacity of CNAC was decreased with increased IR from 1:1 to 2:1 before increased at IR of 3:1. CNAC with 3:1 ratio managed to adsorb 30.9 mg/g of MB at equilibrium. Higher IR was favorable for enhancing the MB adsorption as more pores are developed on the sample surface [9].

Adsorption Isotherm

The most appropriate correlation for the equilibrium curve needs to be established in order to understand the adsorption system. Therefore, the equilibrium adsorption data were analyzed using the Langmuir and Freundlich isotherms as shown in Figure 3 whereas Table 2 summarizes all the constants from both isotherm models.

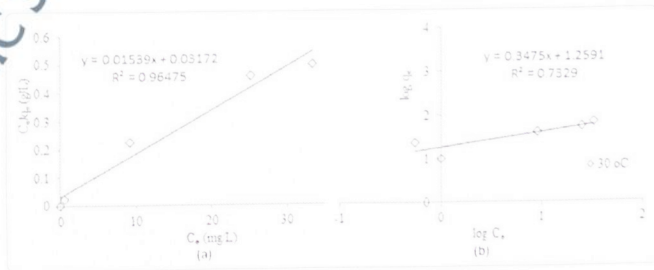


Fig. 3: Linear plots of (a) Langmuir and (b) Freundlich adsorption models

Table 2. Parameters of Langmuir and Freundlich adsorption isotherm for MB.

	Equation	R ²	q _m	K _L	K _F	n
Langmuir	y = 0.0154x + 0.0317	0.965	64.98mg/g	0.152	/	/
Freundlich	y = 0.3475x + 1.2591	0.733	/	/	3.52	2.88

Langmuir model gave the highest R^2 values which were greater than 0.96. Conformation of the experimental data into the Langmuir isotherm equation proved that the surface of CNAC for MB adsorption was made up of homogeneous adsorption patches with monolayer coverage of MB onto CNAC [9]. The monolayer saturation capacity of CNAC was found to 64.98 mg/g at 30 °C.

Adsorption Kinetics

All the experimental and calculated q_e values obtained from the pseudo-first-order and pseudo-second-order kinetic model for adsorption of MB at 30 °C are tabulated in Table 3. Comparing the R^2 values, pseudo-second-order model showed a significant agreement with adsorption mechanisms, which indicated the chemisorption with the heterogeneous active sites occurred on the surface of CNAC [11].

Table 3. Parameter values of the kinetic studies of the adsorption of MB onto CNAC.

MB concentration	Pseudo-first-order			Pseudo-second-order		
	q_e , cal (mg/g)	R^2	K_1	q_e , cal (mg/g)	R^2	K_2
10 mg/L	8.47	0.9721	0.3284	8.45	0.9278	0.1553
25 mg/L	18.46	0.9447	0.6468	25.97	0.9946	0.069
50 mg/L	29.59	0.9343	0.4191	36.63	0.9663	0.0626
80 mg/L	42.60	0.8889	0.231	39.53	0.9876	0.0577
100 mg/L	50.99	0.777	0.1965	45.25	0.9908	0.0575

Conclusion

CNAC was found to be suitable for the removal of MB from aqueous solution. Adsorption of MB was found to increase with increase in contact time and initial dye concentration. The Langmuir isotherm model was well described by the equilibrium data with maximum adsorption capacity of 64.98 mg/g. The pseudo-second-order kinetic model fits well with the kinetic data.

Acknowledgment

The authors are grateful for the funding from Solid Waste Management Cluster, USM (1001/CKT/870023) and research grant from Ministry of Science, Technology and Innovation (MOSTI), Malaysia.

References

1. Atifah N, Saleh R. Removal of methylene blue dye contaminant by combination of ultrasonic and visible light irradiation using perovskite $LaMnO_3$ nanocatalyst. *Materials Science Forum*. 2016; 864: 99-105.
2. Amin N. Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics. *Haz Mater J*. 2009; 165(1-3): 52-62. doi: 10.1016/j.jhazmat.2008.09.067
3. Ghaedi M, GolestaniNasab A, Khodadoust S, Rajabi M, Azizian S. Application of activated carbon as adsorbents for efficient removal of methylene blue: Kinetics and equilibrium study. *Ind Eng Chem J*. 2014; 20(4): 2317-2324. doi: 10.1016/j.jiec.2013.10.007
4. Kumar A, Jena HM. Removal of methylene blue and phenol onto prepared activated carbon from Fox nutshell by chemical activation in batch and fixed-bed column. *Cle Prod J*. 2016; 137: 1246-1259. doi: 10.1016/j.jclepro.2016.07.177
5. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemistry Society*. 1918; 40(9): 1361-1403. doi: 10.1021/ja02242a004
6. Freundlich HMF. Over the adsorption in solution. *Journal of Physical Chemistry*. 1906; 57: 385-470.
7. Langergren S, Svenska BK. Zurtheorie der sogenannten adsorption geloesterstoffe. *Vetenskapsakad. Handlingar*. 1898; 24: 1-39.
8. Ho YS, McKay G. Sorption of dye from aqueous solution by peat. *Chem Engg J*. 1998; 70(2): 115-124. doi: 10.1016/S0949-0467(98)00076-1
9. Ahmad MA, Rahman NK. Equilibrium, kinetics and thermodynamic of Remazol Brilliant Orange 3R dye adsorption on coffee husk-based activated carbon. *Chem Engg J*. 2011; 170(1): 154-161. doi: 10.1016/j.cej.2011.03.045
10. Tan IAW, Ahmad AL, Hameed BH. Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. *Haz Mater J*. 2009; 164(2-3): 473-482. doi: 10.1016/j.jhazmat.2008.08.025
11. Ahmad F, Padi WM, Ahmad MA, Radzi R. Using cocoa (*Theobroma cacao*) shell-based activated carbon to remove 4-nitrophenol from aqueous solution: Kinetics and equilibrium studies. *Chem Engg J*. 2011; 178: 461-467. doi: 10.1016/j.cej.2011.10.044

Removal of methylene blue from aqueous solution using cocoa (Theobroma cacao) nib-based activated carbon treated with hydrochloric acid

Khairul Adli Nikman^{a, c}, Faisal Ahmad^b, Mohd Sukri Hassan^{a, *}

^a Faculty of Science and Technology, Universiti Sains Islam Malaysia, 71800 Bandar Baru Nilai, Negeri Sembilan, Malaysia

^b Cocoa Innovative and Technology Centre, Malaysian Cocoa Board, Lot 12621, 71800 Bandar Baru Nilai, Negeri Sembilan, Malaysia

^c Department of Forensic Medicine, Hospital Kuala Lumpur, 50586 Kuala Lumpur, Malaysia

* Corresponding author: mohdsukri@usim.edu.my

Article history

Received 3 October 2018 Revised

18 January 2018

Accepted 10 April 2018

Published Online 4 June 2018

Abstract

Chemical activation process was applied to prepare a cocoa nib-based activated carbon using potassium carbonate (K_2CO_3). The performance of the activated carbon in removing Methylene Blue from aqueous solution was investigated by batch adsorption studies. The adsorptive properties were studied in terms of initial concentration (C_0 : 100-300 mg/L) and contact time effects. The experimental isotherm data fitted well the Langmuir and Temkin models. The adsorption kinetic followed the pseudo-second-order model and Boyd model explained the mechanism of adsorption. The results indicate that the chemically produced activated cocoa nib carbon has significant potential to be used as an adsorbent material for adsorption of Methylene Blue from aqueous solution.

Keywords: Cocoa nib-based activated carbon, Methylene Blue, Langmuir model, Temkin model, Boyd model

© 2018 Penerbit UTM Press. All rights reserved

INTRODUCTION

The cellulosic originated precursors have been continually explored and tested as adsorbents. This is due to the fact that they possess significant values: abundant in nature, cheap, renewable and comparable with the conventional and commercial adsorbents (Lim and Aris, 2013). Agricultural wastes or by-products are an alternative source to be exploited in order to overcome issues on expensive precursor, regeneration and the effect of regeneration on adsorption capacity (Oladoja *et al.*, 2008). Study on low cost and non-conventional adsorbent could offer significant opportunities for environmental sustainability and at the same time, recommend promising benefits to commercially transform the waste into promising prospects (Ahmad *et al.*, 2012).

Some of the precursors used in the production of cellulosic-based or agricultural waste-based activated carbons in the recent past are cocoa shells (Ahmad *et al.*, 2012; Mylsamy and Theivarasu, 2012), cocoa pod (Pua *et al.*, 2014; Bello and Ahmad, 2011), peanut shells (Wu *et al.*, 2013), rice straw (Kamangkoon *et al.*, 2016), papaya seeds (Collin and Lee, 2008), olive stones (Larous and Meniai, 2016), coconut husk (Tau *et al.*, 2008), coconut mesocarp (Ferreira *et al.*, 2015), beet pulp (Dursun *et al.*, 2005) and avocado kernel seed (Rodrigues *et al.*, 2011). All of these carbons were successfully applied for the removal of contaminants from aqueous solution.

Contaminants such as dyes normally accumulate and remain in the environment for a substantial period due to their resistance to chemical and photo degradation. They have the potential to inhibit sunlight penetration and consequently jeopardise the living of aquatic organisms (Ahmad *et al.*, 2012). Such dyes are Methylene Blue, Basic Red 29 and

Basic Yellow 28 which classify as cationic dyes. Therefore, physical and/or chemical management methods have to be used to remove the dyes from the water system. The use of activated carbon (AC) is one of the effective solutions (Lim and Aris, 2013).

Cocoa nibs (CN) have not been received serious consideration as sorbent, as it is the main precursor in production of chocolate and other cocoa products. However, there are significantly high amounts of waste during the manufacturing processes. The valuable cocoa precursors are discarded after fermentation process due to some deformities and infections. The cocoa nibs are also discarded during winnowing process when the breaking process of the beans result in small fragmented cocoa nibs, which will be blown away during the process. The aim of this work is to convert cocoa nibs into activated carbon, in order to make better use of this agricultural waste. Therefore, the focus of this research was to evaluate the adsorption potential of the cocoa nib-based activated carbon (CNAC) in removing Methylene Blue (MB) from aqueous solutions.

EXPERIMENTAL

Materials

Potassium carbonate (K_2CO_3 , System, 99.5 %) was used as the chemical activating agent, and hydrochloric acid (HCl, Merck, 30 %) and sodium hydroxide (NaOH, Essex, 99 %) were used in pH balancing process. Commercial MB ($C_{16}H_{18}N_3S \cdot 3H_2O$) textile dye was obtained from Sigma-Aldrich (M) Sdn Bhd, Malaysia. De-ionized water was used to prepare all reagents and solutions.

Preparation of deash activated carbon from cocoa nibs

CN used for the preparation of activated carbon was obtained from Cocoa Innovative and Technology Centre, Cocoa Board Malaysia, Nilai, Negeri Sembilan, Malaysia. CN was washed with water to remove dirt and later dried at 105 °C for 24 hours to remove the moisture. 60 g of the dried CN was ground into small particles and sieved to the desired particle size of 0.5 mm. The particles were then loaded into a stainless steel vertical tubular reactor (I: 130 cm, d: 38 mm of 310 grade stainless steel) placed in a tubular furnace (Model Carbolite VST 12 110 900). Carbonization was carried out at 700 °C with heating rate of 10 °C min under purified nitrogen flow at a rate of 150 cm³ min for one hour.

In the second step, approximately 10.0 gram of char was impregnated with 10.0 gram of K₂CO₃ before activated under the same condition to a final temperature of 800 °C for one hour. The activated carbon produced, referred to as CNAC, was then cooled down under nitrogen flow until it reached a room temperature. The impregnation step was repeated with a combination of 10.0 gram char – 20.0 gram K₂CO₃ and 10.0 gram char – 30.0 gram K₂CO₃ to achieve the desired ratios (1:1, 1:2 and 1:3). Then the CNAC was washed with hot deionized water for a few rounds and followed with 0.1 M hydrochloric acid and 0.1 M NaOH until the pH of washing solution reached approximately 6.5 – 7.0. The washing procedure was applied in order to remove the remaining K₂CO₃ (Adinata *et al.*, 2007) and, HCl and NaOH were used to adjust the pH.

Subsequently, the produced activated carbon was added into 250 mL beaker which contained 1 M of HCl, as a leach agent to remove minerals and ash from the carbon (Ahmad *et al.*, 2013). A continuous controlled heat was supplied to the mixture by using a magnetic stirrer with heating ceramic plate (IKA® C-MAG HS7, Germany). The temperature controller was used to maintain a constant temperature (50 °C) for one hour. A thermometer was placed in the beaker to monitor the temperature in real-time. After finished, the de-ash activated carbon was washed with hot deionized water and the pH was adjusted to 6.5 – 7.0 with HCl (0.1 M) and NaOH (0.1 M). Fig. 1 summaries the process in a schematic diagram.

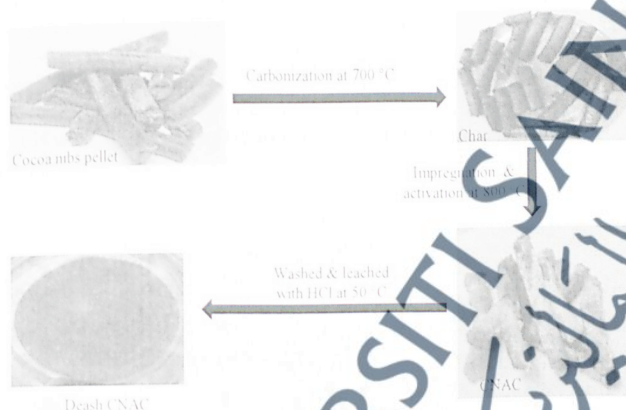


Fig. 1 Schematic diagram for preparation of deash cocoa nib-based activated carbon (de-ash CNAC).

Surface area and porosity analysis of CNAC

The prepared samples (activated carbon) were characterized by N₂ gas adsorption using a Micromeritics ASAP 2010 surface area and porosity analyzer to measure its surface area and porosity. Prior analysis, the sample was degassed at 300 °C until evacuation was completed at 950 mmHg.

Surface functional groups analysis

Surface functional groups were determined using FTIR spectra which were recorded between 4000 and 400 cm⁻¹ using an Agilent 630 FTIR spectrometer. US Diamond ATR accessory was attached to the unit to perform a fast and simple collection of infra red (IR) spectrum. The analysis was performed automatically by MicroLab PC software attached to the system and data handling was assisted by ResPro.

Morphological analysis

Scanning electron microscope (SEM) was used to study the surface morphology of the precursors, chars and the activated carbon prepared including the pore structure, surface structure and pore arrangement. The analysis on surface morphology of the precursor, char and the produced activated carbon was performed using SEM (Model FEI Quanta 450, US).

Batch equilibrium studies

Batch equilibrium studies were carried out by adding a fixed amount of AC (0.60 g) each into each 250 mL Erlenmeyer flasks containing 100 mL of different concentrations (50–400 mg/L) of dye solution. The flasks were agitated in an isothermal water-bath shaker at 120 rpm and 30 °C until equilibrium was reached. Subsequently, the adsorbent was removed from the solution by filtration. The percentage removal of MB was calculated using (1) and the amount of adsorption at time (t), q_t (mg/g) was calculated using (2).

$$\% \text{ Removal of MB} = \frac{C_i - C_t}{C_i} \times 100 \quad (1)$$

$$q_t = \frac{C_i - C_t}{W} \times V \quad (2)$$

where C_i is the initial liquid-phase concentration of dye (mg/L), C_t is the equilibrium liquid-phase concentration of dye (mg/L), C_0 is the initial liquid-phase concentration of dye (mg/L), C_t is the liquid-phase concentration of dye at any time, t (mg/L), V is the volume of the solution (L), and W is the mass of dry adsorbent used (mg).

The final concentrations of the dye were measured using a double beam UV-Vis spectrophotometer (Model Cary 60 UV-Vis, Agilent, US) at the λ_{max} value (668 nm).

Batch kinetics studies

Similarly, the kinetics experimental procedures were identical to those of batch equilibrium studies. The aqueous samples with the adsorbent were agitated until equilibrium reached. The concentrations at different time intervals were taken and were measured similarly. MB removal at equilibrium (q_e , mg/g), was calculated using (2).

RESULTS AND DISCUSSION

Characteristics of activated carbon

Brunauer-Emmett-Teller (BET) surface area, mesopore surface area, total pore volume, mesopore volume and pore size of CNAC and de-ash CNAC are described in Table 1.

Table 1 shows the comparison between the CNAC and the acid (1 M HCl) treated CNAC. The ash content in CNAC was recorded at 14.77 % of the whole weight, and the de-ash CNAC was left with 3.77 %. The pore diameter was increased in de-ash CNAC compared with untreated CNAC which was from 4.93 to 5.52 nm (12 % increment). Other properties were also increased such as BET (47 %), mesopore surface area (64 %), total pore volume (65 %) and mesopore volume (40 %). Therefore, de-ash CNAC contained higher BET surface area and total pore volume compared with CNAC (1.932 m²/g and 2.67, respectively) due to increasing of pore size.

The differences between both BET surface areas and total pore volumes were due to the acid leaching process. Similar observation was reported by Ahmad *et al.*, (2013) where they suggested that acid treatment develops new structure that highly mesoporous. Acid treatment resulted in development of new structure that is highly mesoporous through elimination of carbonates and formation of amorphous silica (Ahmad *et al.*, 2013).

The changes in porosity were due to the dissolution of cations from the AC, which degraded the highly microporous structure to low microporous. The cation dissolution could lead to pore walls destruction which can create new pores and can reduce the density of the treated AC (Ahmad *et al.*, 2013).

Fig. 2 (a) and (b) show the SEM micrographs of both the untreated CNAC and acid treated CNAC (de-ash) samples, respectively. In both

(a) and (b), it can be observed that pores were developed on both surfaces. There were several pores formed on the CNAC surface but the surface of the de-ash CNAC contained more pores. This variation is believed due to the fact that the organic compounds were driven off after combustion however the silica remains were still available in the char structure. The treatment of hydrochloric acid ensures that silica was removed and more pores were obtained. The SEM results showed that the surface activated carbon which was treated with acid contains more well-developed pores where can provide a good surface for MB to be trapped and adsorbed (Hanum *et al.*, 2017).

Table 1 Surface characteristics, proximate contents, and elemental analyses of char, CNAC and de-ash CNAC.

Properties	CNAC	De-ash CNAC
BET surface area (m ² /g)	1,313.88	1,932.36
Mesopore surface area (m ² /g)	400.34	659.60
Total pore volume (cm ³ /g)	1.62	2.67
Mesopore volume (cm ³ /g)	30.47	42.68
Pore diameter (nm)	4.93	5.52
Ash content (%)	14.77	3.77

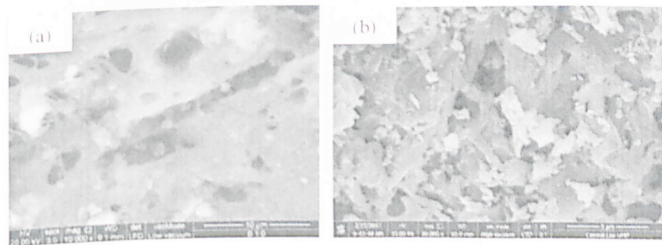


Fig. 2 (a) and (b) show the SEM micrographs of (a) untreated CNAC and (b) acid treated CNAC samples.

Fig. 3 shows the spectrum of the activated carbon samples (CNAC and de-ash CNAC). Both activated carbons developed a similar spectrum and exhibit similar peaks. There is no reduction in both spectrums between 3500 and 800 cm⁻¹ except for a very weak band at 1570 cm⁻¹ in (a), which was disappeared in (b). Result indicated that the acid treatment was not significant in altering the surface functional groups in the CNAC.



Fig. 3 (a) and (b) show the SEM micrographs of (a) untreated CNAC and (b) acid treated CNAC samples.

Batch Adsorption Studies

The adsorption isotherm shows the distribution of adsorption molecules between MB and the de-ash CNAC at an equilibrium state. The adsorption data was fitted to Langmuir, Freundlich and Temkin isotherm models to determine the suitable adsorption model (Rahimi and Vadi, 2014). The amount of MB adsorbed at the equilibrium time specifies the maximum adsorption uptake of the de-ash CNAC as shown in Fig. 4. This happened because of the abundant vacant sites on the adsorbent surface that were available for adsorption during the initial stage (Ahmad *et al.*, 2012).

The adsorption data were investigated using Langmuir, Freundlich and Temkin isotherms. These isotherm models were explained by equation (3), (4) and (5), respectively (Abdel-Ghani *et al.*, 2016):

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} \quad (3)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

$$q_e = \ln K_T + B \ln C_e \quad (5)$$

Using the linear form of the equations, the MB adsorption equilibrium of Langmuir, Freundlich and Temkin have been successfully plotted as shown in Fig. 5, 6 and 7, respectively. Table 2 summaries the values of MB isotherms constants calculated from the developed plots.

The essential characteristic of the Langmuir-type adsorption process can be signified with the dimensionless constant or separation factor, R_L which has a value of $0 < R_L < 1$, where lower R_L value indicates a favorable isotherm adsorbate/adsorbent (Ahmad *et al.*, 2012). The R_L is defined by equation (6) (Chowdury *et al.*, 2011):

$$R_L = \frac{1}{1 + K_L C_i} \quad (6)$$

where K_L is the Langmuir constant (L/mg) and C_i is the highest initial concentration (mg/L).

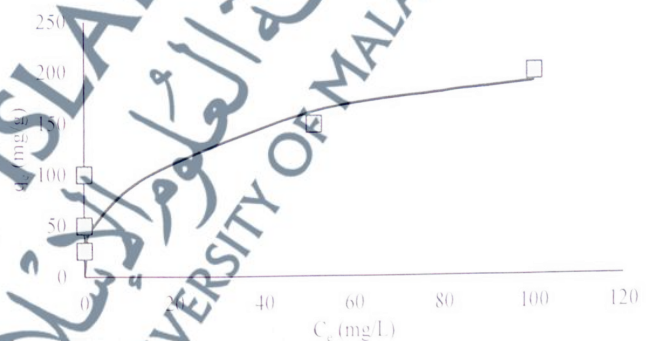


Fig. 4 Equilibrium adsorption of MB onto de-ash CNAC at 30 °C.

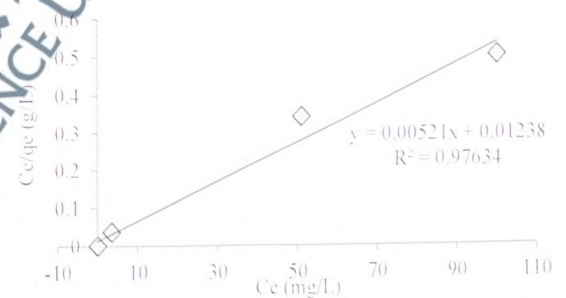


Fig. 5 Langmuir adsorption of MB onto de-ash CNAC.

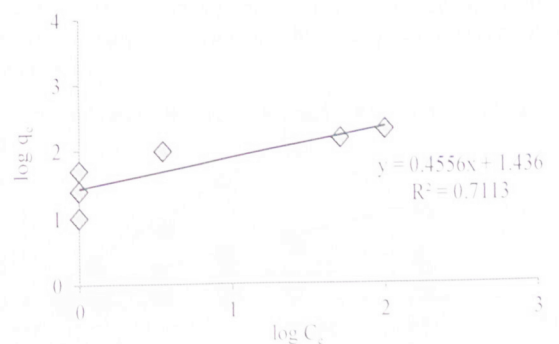


Fig. 6 Freundlich adsorption of MB onto de-ash CNAC.

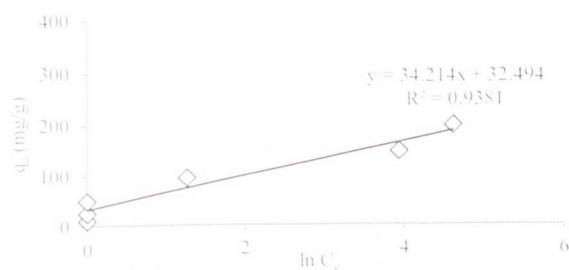


Fig. 7 Temkin adsorption of MB onto de-ash CNAC.

The adsorption data were well fitted with Langmuir isotherm model where the correlation coefficient, R^2 value is close to 1 (0.9763). The higher correlation coefficient of 0.9763 for the Langmuir isotherm predicts the monolayer coverage of MB on the de-ash CNAC particles. A high value of K_L (0.4208) and a low value of R_L (0.0232) indicated a favorable solute adsorbent adsorption process (Joseph and Xavier, 2013).

The Freundlich isotherm did not fit the data well, as the R^2 value is far from 1. The R^2 value for Temkin isotherm is higher than Freundlich but lower than Langmuir, indicating agreement with the experimental data (Ahmad *et al.*, 2012).

Table 2 Isotherm constants for adsorption of MB by CNAC.

Langmuir	R^2	q_m (mg/g)	K_L (L/mg)	R_L
	0.97634	191.94	0.4208	0.0232
Freundlich	R^2	$1/n$	n	K_f ((mg/g)(mg/L) ^{1/n})
	0.7113	0.4556	2.1949	4.2038
Temkin	R^2	A (L/g)	B	-
	0.9381	2.585	34.214	-

The fact that the Freundlich isotherm did not fit the experimental data well may be due to a result of homogeneous distribution of active sites onto the cocoa nib-based activated carbon surface rather than heterogeneous distribution. The Freundlich equation assumes multilayer adsorption on the surface as well as heterogeneous adsorption (Dogan *et al.*, 2006). That is why the data were well fitted with Langmuir but not Freundlich isotherm model.

Table 3 lists other adsorbents with maximum monolayer adsorption capacity of MB. It can be observed that the de-ash CNAC had a relatively moderate adsorption capacity of 191.94 mg/g and nearly similar with cocoa shells (212.77 mg/g).

Table 3 Comparison of the maximum monolayer adsorption of Methylene Blue onto various adsorbents.

Adsorbent	Maximum monolayer, q_m (mg/g)	Reference
Cocoa shell	212.77	Ahmad <i>et al.</i> , 2012
Pecan nutshell	400.06	Bello-Huitle <i>et al.</i> , 2010
<i>Crescentia</i> <i>cujete</i> fruit shell	66.67	Joseph and Xavier, 2013
<i>Jatropha curcas</i> fruit shell	499.17	Tongpoothorn <i>et al.</i> , 2011
Pistachio hull	389.00	Moussavi and Khosravi, 2011
<i>Ricinus communis</i> epicarp	62.50	Santhi and Manonmani, 2009
Cola nuts hell	87.12	Nsami and Mbadcam, 2013
Cocoa nibs	191.94	This work

Adsorption Kinetic Studies

The pseudo-first-order and pseudo-second-order kinetic models were applied to evaluate the kinetic of adsorption of MB on de-ash CNAC. The pseudo-first-order and pseudo-second-order kinetic models were applied to evaluate the kinetic parameters of the adsorption process (Lagergren, 1998). The pseudo-first-order and the pseudo-second-order equations based on equilibrium adsorption are expressed as in equation 7 and 8, respectively (Ho and McKay, 2000):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

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

Fig. 8 demonstrates the pseudo-first-order kinetic model to predict sorption kinetics. The values of K_1 and correlation coefficient, R^2 obtained from the plots for MB adsorption on the activated carbon are given in Table 4. The experimental q_e values were not in agreement with the calculated values obtained from the linear plots. In addition, lowest initial concentration (10 mg/L) did not achieved high R^2 (0.812) values for MB adsorption.

Besides, it was observed that all initial dye concentrations, except for 10 mg/L, the adsorption data were well represented by the pseudo first-order model only the first 30 to 40 minutes. This result suggests that the MB adsorption onto de-ash CNAC does not conform with the pseudo first-order adsorption model. The similar findings have also been observed in the adsorption of MB onto *Crescentia cujete* fruit shell (Joseph and Xavier, 2013), Kenaf core fiber (Sajid *et al.*, 2011) and palm kernel coat (Oladaja *et al.*, 2009). The model is generally not applicable to be used for the whole range of contact time but only effective over the initial 30 minutes of the adsorption processes (Bulut *et al.*, 2008). The result showed that the adsorption of MB on the cocoa nib-based activated carbon was not first-order.

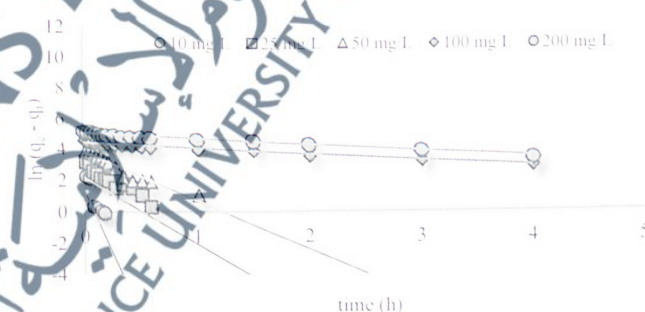


Fig. 8 Pseudo-first-order of MB kinetic adsorption.

Fig. 9 shows a linear plot of t/q_t versus t to represent the pseudo-second-order kinetic model. The graph showed good agreement between the experimental and the calculated q_e values, as addressed in Table 4. The correlation coefficients (R^2) for the linear plots of t/q_t against t were observed to be close to 1 indicating the applicability of the second-order kinetic model to describe the MB adsorption process on the de-ash CNAC. It is clearly suggest that the adsorption kinetic of the MB was accurately described by the pseudo second-order adsorption model.

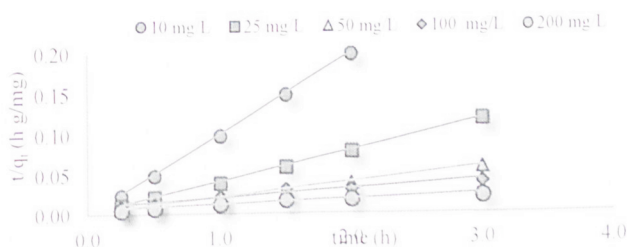


Fig. 9 Pseudo-second-order of MB kinetic adsorption.

From Table 4, it was learn that the R^2 values for second-order model were higher than the first-order model. The higher R^2 value confirmed that the sorption data are well represented by pseudo-second-order kinetics model (Dogan *et al.*, 2004).

Table 4 Kinetics model equation constants and correlation coefficients for MB adsorption.

Initial conc. (mg/L)	Kinetic models					
	Pseudo-first-order			Pseudo-second-order		
	q_0 , cal (mg/g)	K_1 (1/h)	R^2	q_0 , cal (mg/g)	K_2 (g/mg h)	R^2
10	8.711	15.369	0.812	10.000	0.000	1.000
25	19.508	4.081	0.916	25.641	0.691	0.995
50	43.654	3.087	0.963	52.356	0.159	0.995
100	83.188	0.390	0.963	87.719	0.014	0.942
200	160.871	0.397	0.969	158.730	0.007	0.945

*conc. - concentration

CONCLUSION

The CNAC was optimised using hydrochloric acid as leaching agent to remove remaining minerals that contribute to ash content. The de-ash CNAC was used to remove MB. The acid treatment was found to significantly increase the adsorption of MB. The treated carbon was characterized by nitrogen adsorption isotherm to determine its BET surface area, mesopore surface area, total pore volume, mesopore volume and average pore size and the values were 1,932.36 m²/g, 659.60 m²/g, 290.03 m²/g, 2.67 cm³/g, 42.68 % and 5.52 nm, respectively. The acid treatment process did not influence the composition of functional groups in the CNAC. The adsorption kinetics indicated that pseudo-second-order kinetic model fits the adsorption data, while the adsorption isotherm was well explained by Langmuir and Temkin isotherm models. The results of this study demonstrate that the adsorption capacity of CNAC can be optimized by hydrochloric acid treatment.

ACKNOWLEDGEMENT

This work was financially supported by the Malaysian Cocoa Board (MCB) under the Research Grant from Ministry of Science, Technology and Innovation (MOSTI), Malaysia.

REFERENCES

- Adinata, D., Wan Daud, W. M. A., Aroua, M. K. 2007. Preparation and characterization of activated carbon from palm shell by chemical activation with K₂CO₃. *Bioresource Technology*, 98, 143-149.
- Ahmad, F., Wan Daud, W. M. A., Ahmad, M. A., Radzi, R. 2013. The effects of acid leaching on porosity and surface functional groups of cocoa (*Theobroma cacao*)-shell based activated carbon. *Chemical Engineering Research and Design*, 1028-1038.
- Ahmad, F., Wan Daud, W. M. A., Ahmad, M. A., Radzi, R. 2012. Cocoa (*Theobroma cacao*) shell-based activated carbon by CO₂ activation in removing of Cationic dye from aqueous solution: Kinetics and equilibrium studies. *Chemical Engineering Research and Design*, 1480-1490.
- Bello, O., Ahmad, M. A. 2011. Adsorptive removal of a synthetic textile dye using cocoa pod husks. *Toxicological & Environmental Chemistry*, 93(7), 1298-1308.
- Bulut, E., Ozacar, M., Sengil, I. A. 2008. Adsorption of malachite green onto bentonite: Equilibrium and kinetic studies and process design. *Microporous and Mesoporous Materials*, 234-246.
- Chowdhury, Z., Mohd Zain, S., Atta Khan, R., Khalid, K. 2011. Linear regression analysis for kinetics and isotherm studies of sorption of manganese (II) ions onto activated palm ash from waste water. *Portugal Journal of Chemistry*, 27(2), 405-415.
- Collin, J., Lee, M. 2008. Sorption kinetic studies of medical grade activated carbon prepared from papaya seeds. *Modern Applied Science*, 2(6), 115-123.
- Dogan, M., Alkan, M., Turkyilmaz, A., Ozdemir, C. 2004. Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *Journal of Hazardous Materials*, B109, 141-148.
- Dursun, G., Cicek, H., Dursun, A. 2005. Adsorption of phenol from aqueous solution by using carbonised beet pulp. *Journal of Hazardous Materials*, 125(1), 175-182.
- Ferreira, R., Couto Junior, O., Carvalho, K., Arroyo, P., Barros, M. 2015. Effect of solution pH on the Removal of paracetamol by activated carbon of dende coconut mesocarp. *Chemical and Pharmaceutical Engineering Quarterly*, 47-53.
- Hanun, F., Bani, O., Wihini, L. 2017. Characterization of activated carbon from rice husk by HCl activation and its application for lead (Pb) removal in car battery wastewater. *Materials Science and Engineering*, 180.
- Joseph, J. A., Xavier, S. 2013. Equilibrium and kinetic studies of Methylene blue onto activated carbon prepared from C. escentia elite fruit shell. *Nature and Science*, 54-58.
- Kumar, P., Kirthika, K. 2009. Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto coal fly ash powder. *Journal of Engineering Science and Technology*, 4(4), 351-365.
- Larous, S., Memari, A.-H. 2010. Adsorption of Dichlorane from aqueous solution using activated carbon prepared from olive stones. *International Journal of Hydrogen Energy*, 10350-10390.
- Lim, A., Aris, A. 2015. A review on economically adsorbents on heavy metals removal in water and wastewater. *Reviews in Environmental Science and Technology*.
- Malsamy, S., Theivarasu, E. 2012. Adsorption of reactive dye using low cost adsorbent: Cocoa (*Theobroma cacao*) Shell. *World Journal of Applied Environmental Chemistry*, 22-29.
- Oladojo, N., Asin, L., Aboluwajo, C., Oladimeji, Y., Ashogbon, A. 2008. Studies on the sorption of basic dye by rubber (*Hevea brasiliensis*) Seed Shell. *Turkish Journal of Engineering and Environmental Sciences*, 32, 143-152.
- Pua, F., Sajab, M., Chua, C., Zakaria, S., Abdul Rahman, I., Salit, M. 2013. Alkaline-treated cocoa pod husk as adsorbent for removing methylene blue from aqueous solutions. *Journal of Environmental Chemical Engineering*, 1, 460-465.
- Rahimi, M., Vafaei, M. 2014. Langmuir, Freundlich and Temkin adsorption isotherms of propranolol on multi-wall carbon nanotube. *Journal of Modern Drug Discovery And Drug Delivery Research*, 1-3.
- Ramangkron, S., Saenjum, C., Sirithunyalug, B. 2016. Preparation of rice straw activated charcoal by 2-step H₃PO₄ activation. *International Journal of Pharmacy and Pharmaceutical Sciences*, 8(4), 218-221.
- Rodrigues, L., da Silva, M., Alvarez-Mendes, M., Coutinho, A., Tim, G. 2011. Phenol removal from aqueous solution by activated carbon produced from cocado kernel seeds. *Chemical Engineering Journal*, 174(1), 49-57.
- Sajab, M., Chua, C., Zakaria, S., Jani, S., Ayob, M., Chee, K., ... Chiu, W. 2011. Citric acid modified kenaf core fibres for removal of methylene blue from aqueous solution. *Bioresource Technology*, 102, 7237-7243.
- Tan, I., Ahmad, A., Hameed, B. 2008. Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies. *Journal of Hazardous Materials*, 154(1), 337-346.
- Wu, M., Guo, Q., Fu, G. 2013. Preparation and characteristics of medicinal activated carbon powders by CO₂ activation of peanut shells. *Powder Technology*, 188-196.