The Removal of Heavy Metals from Industrial Effluents using Biomass Based Modified Activated Carbon

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ABSTRACT

Modified coconut shell based activated carbon was used as a precursor in this study to remove heavy metals Lead (Pb), Aluminium (Al), Manganese (Mn), Iron (Fe), and Cadmium (Cd) from industrial effluent using the thermal process of pyrolysis and carbonization for 2 hr and impregnation ratio of 1:2 with phosphoric acid (H_3PO_4) and sodium hydroxide(Na_OH) for three different biomass particle size at 600^0c temperature using $Znlc_2$ as an activating agent. A maximum activated carbon yield of 68g was obtained for the coconut shell. The optimum activation temperature, impregnation ratio, time, uptake capacity and removal rate were determined. The results of this work illustrates that high-quality activated carbon can be locally manufactured from coconut shell waste, and a scale-up of this production will go a long way in reducing the tons of coconut shell waste generation in the country.

1. INTRODUCTION

Activated carbon (AC) has attracted a lot of interest in industrial applications such as water treatment (Bentil & Buah, 2016), mining (Buah et al., 2016), energy storage (Mohammed et al., 2018), purification of gases (Hidayu & Muda, 2016), medicine, sewage treatment, and filters.

The use of AC in these industries is possible due to its exceptional mechanical property, high porosity, high surface area, the presence of organic/ inorganic functional groups etc. The properties found in AC are influenced by the precursor and the manner of activation used in its preparation (Abechi et al, 2013; Romeo Anaya et al., 2012)

Industrial discharge contains various organic and inorganic pollutants. Among these pollutants are heavy metals which can be toxic and/or carcinogenic and which when consumed by humans and other living organisms can be harmful (MacCarthy etal.1993; Clement et al.1995; Renge et al. 2012). The heavy metals of most alarm from various industries include lead (Pb), zinc (Zn), copper (Cu), arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni) and mercury (Hg) (Mehdipour et al. 2015). They instigate from sources such as metal complex dyes, pesticides, fertilisers, fixing agents (which are added to dyes to improve dye adsorption onto the fibres), mordants, pigments and bleaching agents (Rao et al. 2010). In developed countries, legislation is becoming increasingly stringent for heavy metal limits in wastewater.

The infiltrating wastewater picks up a large number of heavy metals and grasps the aquifer system and pollutes groundwater. Health risks of heavy metals include reduced growth and development, cancer, organ damage, nervous system damage and, in extreme cases, death. Heavy metals become toxic when they are absorbed by the body and accumulate in the soft tissues (Malassa et al. 2014).

Numerous researches have been conducted as well as the production of activated carbon from waste biomass such as date stone (Bouchelta et al. 2008), durian shell (Chandra et al. 2009), soybean oil cake (Tay et al. 2009), cherry stone (Marin et al. 2009), palm shell and coconut shell (Daud & Ali 2004). These byproducts need to be managed so it does not become impracticable waste. Nowadays, many resolutions have been found for the processing of solid waste, ranging from making fertilizers biobriquettes, souvenirs and even making environmentally responsive alternate energy.

Higher temperatures are a disadvantage in the scale-up of the production of activated carbon and a better and cost-effective method is required to produce activated carbon industrially. The activation process is the key in the production of activated carbon. The shape and the size of pores in the AC is influence by either chemical or physical activation. Chemical activation involves one step process by saturating the precursor with a chemical reagent followed by roasting or heating under unreactive conditions. Chemical activation generates AC with high yield, high surface area, high and employing lower temperature. Quite a number of the inorganic chemical agent has been used in the activation of AC. The most frequently used are KOH, $ZnCl_2$ - , H_3PO_4 - and Na_OH (Willams & Reed, 2004; Singh et al., 2013; Pragya et al., 2013). Generally, the precursors for commercially available AC are derived from petroleum remains coal, wood, lignite, and peat which are very expensive and likely to run out (Ahmedna et al., 2000). As a result, the focal point has been shifted to agricultural waste materials which are environmentally responsive, effective and cheaper. Although the carbon yield of AC produced from these agricultural waste materials is lower compared to those obtained from coal or peat, their environmental, sustainability and economic impact can counterbalance the treatment and disposal cost of using peat and coal.

The adsorbents are easily generated and separated from the mixture (Ali et al. 2019). A number of natural and synthetic adsorbents belonging to different sources have been applied for the adsorption of different metals from wastewater effluents. However, they do not fulfil the requirements of low cost and high efficiency especially for the removal of toxic substances. Therefore, preparation of highly efficient materials with a wide range of applicability, easy reversibility and low cost for the adsorption of a wide range of heavy metals is extremely important.

Adsorption is considered one of the most effective and low-cost methods to eradicate heavy metals from water (Demey et al. 2018). It is an environmentally friendly technique with flexibility in design and operation. The process of adsorption is reversible and the adsorbents can be regenerated through desorption of the adsorbed species. Meanwhile, different types of biological, agricultural and industrial materials and mineral oxides have been applied with high efficiency for the removal of heavy metals (Chammui et al. 2014; Saleh et al. 2016).

However adsorption method classically uses activated carbon from a raw material that have high carbon content. However, the rich supply of coconut shell as a waste-product from the coconut oil and desiccated coconut industry makes production of activated carbon from this material more financially feasible since using grain or coal as raw materials for activated carbon will necessitate manufacturers extra amount of money for procurement. Moreover, besides being an unstructured form of carbon that can absorb many gases, vapours, and colloidal solids, coconut shell activated carbons are expedient over carbons made from other materials because of its high density, high purity, and virtually dust-free nature. These carbons are harder and more resistant to abrasion.

Moreover considerable attention has been focused on removal of pollutants by using adsorbents derived from low-cost agro-wastes that are abundantly found and easily available in the sub Saharan countries generally and particularly Nigeria. Thus, the aim of this study is to develop optimum conditions for the removal of heavy metals from industrial effluent by means of carbonization, H_3po_4 and Na_OH activation. The removal requirement and uptake capacity such as pH, contact time, effect of an adsorbent were determined. The performance of the coconut shell derived adsorbents was compared. The results of those studies provided a better consideration of the mechanism for the adsorption of heavy metals onto the prepared powdered activated carbon.

2. Results and discussion

Analysis: The heavy metals present in the wastewater sample, were analyzed using the atomic-absorption spectrophotometer It detected the concentrations of Pb, Al, Mn, Fe and Cd. The initial concentrations of the metal ions present in the waste water are shown in table 1.

Table 1. Initial concentration of metal ions in wastewater

Heavy metals	Initial concentration (mg/L)
Pb	43.500
Al	16.600
Mn	17.400
Fe	0.005
Cd	16.600

Adsorption Study: Adsorption experiment was done by measuring 50 ml of the wastewater sample and poured into a 100 ml conical flask. 0.2 g of the previously prepared activated carbon was added to the wastewater. The conical flask containing the adsorbent and the wastewater was placed on a rotary shaker and shook at 150 rpm at a room temperature of (32^0C) for a period of 120 min to ensure equilibrium. The suspension was filtered using Whatman filter paper. Atomic adsorption spectro-photometer was used to analyse the concentrations of the different metal ion present in the filtrate. The amount of metal ions adsorbed by the adsorbent was evaluated using equation:

$$qe = \frac{(C0 - Ce)V}{M}$$

2.1 Activation temperature

Heat application further accelerates thermal degradation to an impregnated material and the volatilization process which leads to an increase and development of pores and surface area and subsequent mass loss.

Activation temperature selection depends on several factors which comprise of the precursor type and the chemical agent used. Different biomass precursor's activation temperature varies from 400 to 800^{0}c.(Diao etal 2002) while that of coal based material can go as high as 900^{0}c (karacan etal 2007).

3. METHODS

All the chemicals used in this study were prepared and obtained from the centre for dry land agriculture laboratory Bayero university Kano Nigeria. The coconut shell was obtained around the Naibawa (yanlemo) market in Kano Municipal. This site is the collection point of most of the used coconut shells in the municipality.

3.1 Fabrication of activated carbon from coconut shell:

Coconut shells were dried overnight in an oven at 100^{0}c, coconut shell will have to go through the dehydration course, this process begins with the cleaning of impurities that are still in the coconut shell and such impurities, sand, coconut fibre and epidermis on coconut shells, etc. The dehydration purpose is to remove the water content enclosed in the sample.

The dried sample was cooled at room temperature before proceeding to the next step.fig 1. The precursor was pulverized to the size of 1.70mm, 0.425mm, 0.063mm particle size respectively. Phosphoric acid (acid) and sodium hydroxide solutions (base) were prepared and added into each particle size synchronously to the required impregnation ratio of 1:1 which is defined as the ratio of dry weight of H_3po_4 and NaoH to the weight of the coconut shell.

Based on the study by Molina sabio etal 1995. one hundred and fifty grams of the coconut shell were weighed into a beaker and then impregnated by mixing with 150ml of phosphoric acid and sodium hydroxide respectively for each particle size to obtain a homogenous mixture and left to stand for 24 hrs at ambient condition.

The carbon material was then placed into a crucible then transferred to a muffle furnace at 600^{0}c for 2 hrs for pyrolysis. The selection of temperature is based on numerous experiments carried out, and obtained the perfect results of drying at 600^{0}c, because if the temperature is too high the coconut shell sample will run out and become ash, and when the temperature is too low, carbon will turn out not perfect.

3.2 Preparation of activated carbon

The activation processes to produce activated carbon from carbonaceous materials is of two types, i.e. chemical and physical activation processes. Physical activation method involves a two-step process, i.e. carbonisation, followed by activation using oxygen, carbon dioxide or steam as an activating agent (Yuen & Hameed 2009). Nonetheless, in the chemical activation procedure, carbonisation and activation processes occur in a single stage using chemicals as an activating agent such as phosphoric acid, zinc chloride and potassium hydroxide (KoH). (Ncibi et al. 2009).

Moreover the obtained carbon is set to be activated. In this research, the used activator is $ZnCl_2$. This is based on research journals that use different activators on different ingredients. In this research however coconut shell carbon activator is Zncl2 15%. The activation process was carried out by soaking the carbons into an activator for 24 hrs. The obtained product (activated carbon) will then be washed repeatedly to remove any traces of acids or bases. The activated samples will be neutralized by washing with distilled water until the ph reading is about 6-7 the washed activated carbon will then be placed in an oven with temperature set at 100^0c for 24hrs for drying. The dried material will then be crushed and grounded into small particles and again washed several times with deionised water to remove any traces of any absorbed salts. The prepared activated carbon was then placed in a desiccator for further use. The processes of preparing and synthesizing the coconut shell into PAC are shown in fig 1.

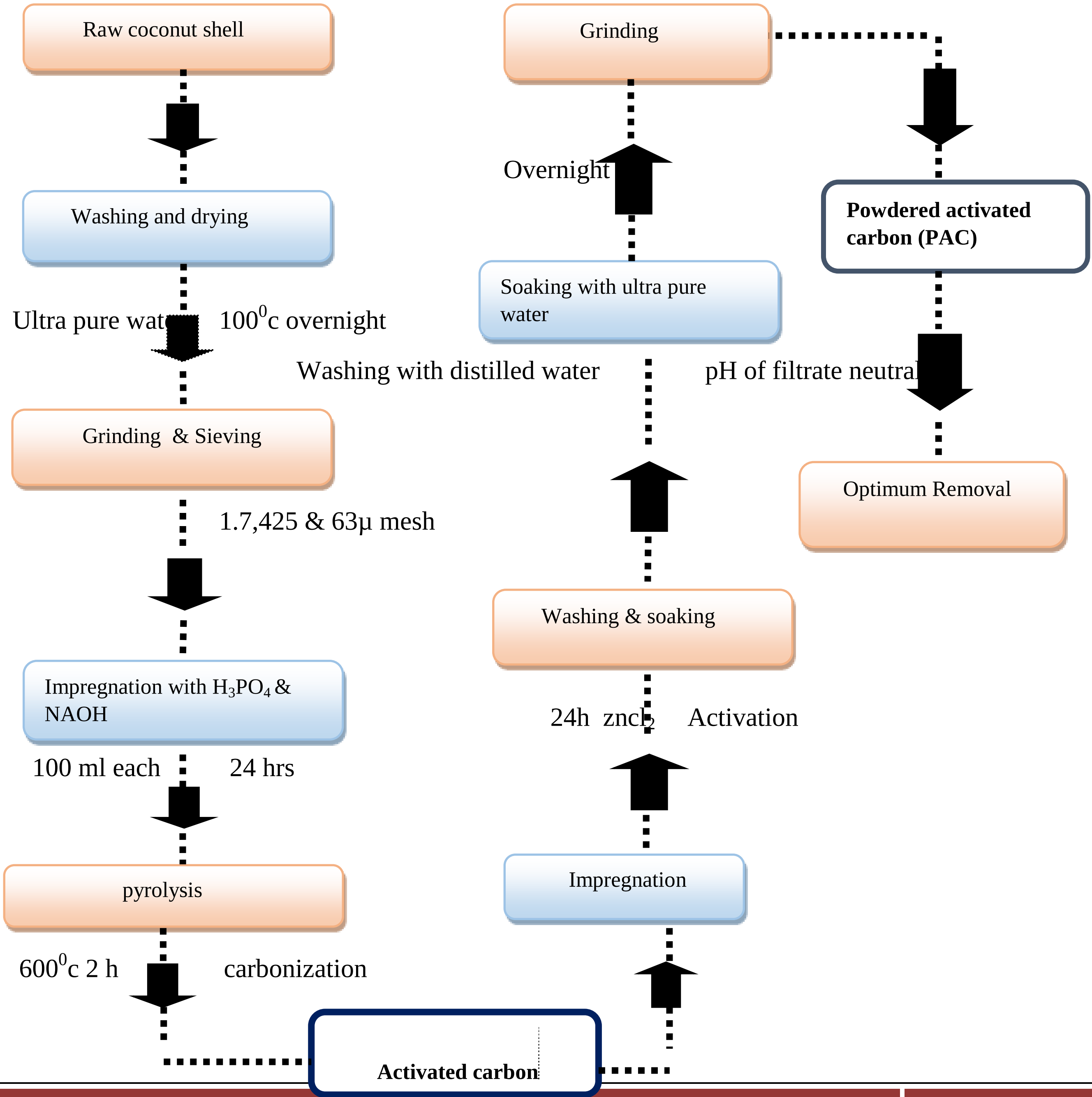

Fig 1 Process for fabrication of PAC from coconut shell.

Effect of temperature

Experiments were performed in the temperature range 20–50^{0}C at constant Pb concentration (10.0 mg/L), adsorbent dose (3.0 g/L), contact time (3.0 h) and pH (3.5 for Mn and 2.0 for Cd and Al). Adsorption of Pb on all the adsorbents witnessed the increase in adsorption percentage and adsorption capacity (*Q*e) from 20^{0}C to 30^{0}C and no significant change with further increase of temperature.

Effect of pH

The effect of pH on heavy metals adsorption affects the interaction between the activated carbon and the heavy metals. The pH of the effluent influences the surface charge of the adsorbent and the ionization of the adsorbate. However, hydrophobic interaction, hydrogen bonds, π-π interaction, and n-π interaction also affect the adsorption performance in the effluent. The highest rate of removal of cadmium was at pH 4, with an uptake of almost 100%. It is effective when removed by the activated carbon at pH 4. The attraction forces between an aqueous solution with low pH (high value of H+ charge).

Effect of contact time

The effect of contact time on heavy metals removal was investigated at optimized adsorbent dose by varying the contact time (20-80 min.), while other parameters were kept constant. Increase in percentage removal was observed with increase in contact time for all adsorbents. Optimum time observed was 60 min. for all adsorbents at which % removal of cadmium was 77.8%(0.3 mm) and 76.4%(1.0mm) for ACS while in case of ACC ,% removal was 72.3% and 66.3% optimized adsorbent dose and contact time by varying pH from 2.0-12.0. Progressive decrease in heavy metals adsorption was observed with increase in pH from 2 to 12 and maximum adsorption was observed at pH 2. AC showed maximum removal i.e. 85 % and 82 % (0.3 mm and 0.1 mm)

Effect of Adsorbent Dosage: Different dosages of the adsorbents (0.2-1g) were added in different conical flasks containing 50 ml of wastewater solution, corked and agitated in
A shaker for 1h at a speed of 150 rotations per minute (rpm) at a room temperature of 32^{0}C. The content of each flask was then filtered and analyzed after the agitation time.

Conclusion

This study set out to optimize the production of AC from agricultural byproduct, coconut shell, from the obtained results, it is evident that activated carbon produced from coconut shell is a good adsorbent for removal of lead, iron, cadmium, aluminium and manganese ions. Batch experiments were conducted and showed that the adsorption of lead, iron, cadmium, aluminium and zinc ions are time dependent, adsorbent dosage dependent, pH dependent, and stirring speed dependent. Coconut shell (a waste) is inexpensive and readily available, thus this study provide a cost effective means for removing metal ions from contaminated water or effluents. Through chemical activation using H_3PO_4. Chemical activation of the coconut shell to produce AC was successfully accomplished in a well-controlled laboratory with the application of appropriate instrumentation. AC produce locally using agricultural waste can be used as a substitute for imported carbon. A successful large-scale implementation of this study will go a long way to reduce the tons of waste generated in the country, reduce the pressure on the local currency due to importation and create jobs for the citizenry.

References

Abechi, S. E., Gimba, C. E., Uzairu, A. & Dallatu, Y. A. (2013) Preparation and characterization of activated carbon from Palm Kernel shell by chemical activation.*Res J Chem Sci* **3** (7), 54 – 61.

Ahmedna, M., Marshall, M.E., Rao, R.M., 2000. Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. Bioresource Technology 71, 113–123.

Ali, H., Khan, E., 2019. Trophic transfer, bioaccumulation, and biomagnification of non-essential hazardous heavy metals and metalloids in food chains/webs—concepts and implications for wildlife and human health. Hum. Ecol. Risk Assess. 25, 1353–1376 org/10.1080/10807039.2018.1469398.

Bentil, J. & Buah, W. K., (2016). Removal of Fluoride in Water Using Activated Carbons Prepared from Selected Agricultural Waste Materials, *Journal of Environment and Earth Science* **6** (4), 146 - 152

Buah, W. K., Fosu, S. & Ndur, S. A. (2016) Abatement of Heavy Metals Concentration in Mine Waste Water sing Activated Carbons Prepared from Coconut Shells in a Gas-Fired Static Bed Pyrolysis/Activation Reactor. *G J T* **1** (1), 46 - 52.

Bouchelta C, MedjramMS, Bertrand O& Bellat JP. 2008. Preparation and characterization of activated carbon from date stones by physical activation with steam. *Journal of Analysis Applied Pyrolysis* 82: 70–77

Chandra TC, Mirna MM, Sunarso J, Sudaryanto Y& Ismadji S. 2009. Activated carbon from durian shell: preparation and characterization. *Journal of Taiwan Institute Chemical Engineering* 40: 457–462

Chammui Y., Sooksamiti P., Naksata W., Thiansem S., Arqueropanyo O.A. (2014): Removal of arsenic from aqueous solution by adsorption on Leonardite. Chemical Engineering Journal, 240: 202–210.

Clement, R. E., Eiceman, G. A. & Koester, C. J. Environmental analysis. Analytical Chemistry 67 (12), 221R–255R.

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

Demey H., Vincent T., Guibal E. (2018): A novel algal-based sorbent for heavy metal removal. Chemical Engineering Journal, 332: 582–595.

Diao, Y., Walawender, W.P., Fan, L.T., 2002. Activated carbons prepared from phosphoric acid activation of grain sorghum. Bioresource Technology 81, 45–52.

Hidayu, A. R. & Muda, N. (2016) Preparation and characterization of impregnated activated carbon from palm kernel shell and coconut shell for CO2 capture. *Procedia Eng* **148**, 106 – 113.

Karacan, F., Ozden, U., Karacan, S., 2007. Optimization of manufacturing conditions for activated carbon from Turkish lignite by chemical activation using response surface methodology. Applied Thermal Engineering 27 (7), 1212–1218.

MacCarthy, P., Klusman, R. W., Cowling, S. W. & Rice, J. A. 1993.Water analysis. Analytical Chemistry 65 (12), 244R–292R.

Malassa H, Hadidoun M, Al-Khatib M, Al-Rimawi F, Al-Qutob M (2014) Assessment of groundwater pollution with heavy metals in North West Bank/Palestine by ICP-MS. J Environ Prot 05(01):54–59. doi:10.4236/jep.2014.51007

Marín MO, Fernández JA, Lázaro MJ, Fernández-González C, Macías-García A, Gómez-Serrano V, Stoeckli F & Centeno TA. 2009. Cherry stones as precursor of activated carbons for supercapacitors. *Material, Chemical and Physical* 114: 323–327.

Mehdipour, S., Vatanpour, V. & Kariminia, H.-R. 2015. Influence of ion interaction on lead removal by a polyamide nanofiltration membrane. Desalination 362, 84–92.

Mohammed, L., Park, J. H., Ko, J. M. & Park, J. (2018) Supercapacitive properties of composite electrode consisting of activated carbon and quinone derivatives. *J Ind Eng Chem*.**63**, 12 – 18.

Molina-Sabio, M., Rodriguez-Reinoso, F., Caturia, F., Selles, M.J., 1995. Porosity in granular carbons activated with phosphoric acid. Carbon 33 (8), 1105–1113.

Ncibi MC, Jeanne-Rose V, MahjoubB, Jean-MariusC, Lambert J, Ehrhardt JJ, Bercion Y, Seffen M & Gaspard S. 2009. Preparation and characterization of raw chars and physically activated carbons derived from marine *Posidonia oceanica* (L.) fibres. *Journal of Hazardous Material* 165: 240–249.

Pragya, P., Sripal S. & Maheshkum Ar, Y. (2013) Preparation and study of properties of activated carbon produced from agricultural and industrial waste shells. *Res J Chem Sci* **3** (12), 12 – 15.

Rao, K. S., Mohapatra, M., Anand, S. & Venkateswarlu, P. 2010 Review on cadmium removal from aqueous solutions. International Journal of Engineering, Science and Technology 2 (7), 81–103.

Renge, V. C., Khedkar, S. V. & Pandey Shraddha, V. 2012 Removal of heavy metals from wastewater using low cost adsorbents: a review. Scientific Reviews and Chemical Communications 2(4), 580–584.

Romero-Anaya, A. J., Lillo-Rodenas, M. A. & Lecea, C. S. M. (2012) Linares-Solano A. Hydro-thermal and conventional H3PO4 activation activation of two natural bio-fibers. *Carbon* **50**, 3158 – 69.

Saleh TA, Danmaliki GI. Adsorptive desulfurization of dibenzothiophene from fuels by rubber tyres-derived carbons: Kinetics and isotherms evaluation. Process Saf Environ Prot 2016; 102:9–19. https://doi.org/10.1016/j.psep.2016.02.005.

Singh, P., Raizada, P., Pathania, D., Sharma, G. & Sharma, P. (2013) Microwave induced KOH activation of guava peel carbon as an adsorbent for congored dye removal from aqueous phase. *Indian J. Chem. Technol*. **20**, 305 – 311.

Tay T, Ucar S & Karagöz S. 2009. Preparation and characterization of activated carbon from waste biomass. *Journal of Hazardous Material* 165: 481–485.

Williams, P. T. & Reed, A. R. (2004) High grade activated carbon matting derived from the chemical activation and pyrolysis of natural fibre textile waste. *J Anal Appl. Pyrol*.**71**, 971 – 86.

Yuen. F. K & Hameed B. A. 2009. Recent developments in the preparation and regeneration of activated carbons by microwaves.149(1-2):19-27. School of chemical engineering, engineering campus universiti sains Malaysia 14300 nibonh tebal penang Malaysia. doi 10.1016/j.cis.2008.12.005