



Production of activated carbon from African star apple seed husks, oil seed and whole seed for wastewater treatment

Olubunmi Grace Abatan, Babalola Aisosa Oni^{*}, Oluranti Agboola, Vincent Efevbokhan, Odedoyin Okiki Abiodun

Department of Chemical Engineering, Covenant University, Ota, Nigeria

ARTICLE INFO

Article history:

Received 17 October 2018

Received in revised form

19 May 2019

Accepted 30 May 2019

Available online 31 May 2019

Keywords:

African star apple

Activated carbon

Phosphoric acids

Waste water and zinc chloride

ABSTRACT

African star apple seed husks, oil seed and whole seed were used for activated carbon production for the treatment and elimination of suspended and dissolved particles from industrial waste water. The activated carbon was produced using chemical activation method with phosphoric acid (H_3PO_4) and zinc chloride ($ZnCl_2$) as the activating agents at a carbonization temperature of 500 °C. The morphological interpretations and functional groups of the activated carbon were observed using scanning electron microscopy and Fourier transform infrared spectroscopy respectively. Results obtained from the various pollution indicators showed an appreciable improvement on the quality of the water. The pH, temperature, total suspended solids, total dissolved solids and biological oxygen demand were determined with variation of the contact time of the activated carbons with the industrial wastewater. Seed husks of zinc chloride and Oil seed of phosphoric acid produced an activated carbon with the highest adsorptive performance for pH, temperature, Total Dissolved solids (TDS), Total suspended solids (TSS) and Biochemical oxygen demand (BOD) removal at 7.01, 7.14; 25.1 °C, 25.0 °C; 24.20 mg/L, 21.09 mg/L; 17.64 mg/L, 15.4 mg/L and 6.28 mg/L, 4.8 mg/L respectively at 150 min and yield of 75.2% and 54.3%.

© 2019 Elsevier Ltd. All rights reserved.

1. Introduction

Activated carbon (AC) can be defined as a type of carbon which has been prepared to make it amazingly permeable in other to have an extensive surface region accessible for adsorption or synthetic responses (Mattson, 1971). The primary concern of AC is the evacuation of compound segment by adsorption from the fluid or gas stage (Bansal, 1988). Activated carbons (ACs) preparation are of two ways, namely: Carbonization of a raw materials and Carbon activation. However, Carbonization involves thermal decomposition of raw materials, thereby removing non-carbon species and creating a fixed carbon mass with a fundamental pore structure (very small and closed pores are created during this step). Furthermore, activation brings about the enlargement of the diameters of small pores thereby creating new pores which can be carried out by either chemical or physical means. All through chemical activation, carbonization and activation are accomplished in a single step by carrying out thermal decomposition of the raw material

impregnated with certain chemical agents such as Phosphoric acids, Nitric acids, Sulphuric acids, Sodium Chloride, Zinc Chloride etc. (Mohammadi et al., 2010). For cases like this, the raw material is treated mainly with a chemical agent by impregnation as a result, the raw material is carbonized at a temperature ranging from 450 to 850 °C at atmospheric condition. One reason for dehydrating is to inhibit tar formation which may not be desired throughout the carbonization process. However, surface area and pore size distribution can be determined by the ratio between the mass of the chemical agent and the raw material. Factors such as carbonization temperature, activation time and heating rates are vital preparation variables for obtaining activated carbons with specific properties (Namasivayam and Kadirvelu, 1997).

Physical activation uses an oxidizing gas (CO_2 , H_2O , O_2 , etc.) for the activation of carbons after carbonization, between 850 and 1,000 °C. Carbonization processes can be carried out in tubular furnaces, reactors, muffle furnace and more recently, in glass reactor placed in a modified microwave oven (Phan et al., 2006). When selecting a precursor, certain factors such as cost, availability and purity must be put into consideration; however, the application of the product and the manufacturing process are also important (Bagheri and Abedi, 2009). When the precursor is been

^{*} Corresponding author.

E-mail address: babalola.oni@covenantuniversity.edu.ng (B.A. Oni).

pyrolysed, a porosity is attained on the char fraction which produces elements such as H₂, O₂ and N₂ in form of gases and tars, thereby leaving a rigid carbon skeleton formed by aromatic structures. In chemical activation, the precursor is first impregnated with a dehydrating agent which is heated in an inert atmosphere (Ahmedna et al., 2000). However, during a physical activation process carbonization of the precursor is done under an inert atmosphere, thereby subjecting carbon to a partial and controlled gasification at high temperature (Olivares-Marín et al., 2006). According to Song et al., (2016), there are two types of heating methods for activated carbon, they include: the conventional heat which results in surface heating from the hearth wall, there is no uniform temperature in this process. The latter is the Microwave heating where heat is been generated from inside the material as the materials receives energy through dipole rotations and ionic conduction. The Brunauer, Emmett and Teller (BET) is another important feature showing the influence of production temperature on the activated carbon properties. Increase in the BET surface area, result to an increase in temperature of activation. This may occur as a result of the development of new pores from volatile matter.

The Surface area of the activated carbon is very important in physical property of activated carbon. Molecular size of the adsorption and the pore diameter of the AC are dependent on the surface area available for specific applications. Due to the essence of rapid diffusion of the liquid they require larger pores making a majority of pores of gas phase adsorbents have 3 mm in diameter and smaller which characterizes the liquid-phase carbons generally. The pressure drop and carbon losses are considered important for the mechanical strength and the resistance of the particles. Grades of AC can be determined by the density of AC, together with its specific adsorptive capacity for a given substance which is required for an existing system. Today, activated carbon has been manufactured from different precursors, for example, Moringa seed husks, rice husk, cherry stones, African star apple seed husks, coconut shells, palm shells, to specify amongst many. Accumulation of a substance at the interface is referred to as the 'adsorption' which occurs between two phases such as a solid and gas or solid and liquid. Adsorbate is the substance which accumulates at the interface while 'adsorbent' is the solid on which the adsorption occurs (Tay et al., 2009). Occurrence of adsorption may result from either the universal van der Waals interactions (physical adsorption, physisorption) or it can have the behaviour of a chemical process (chemisorption) (Srinivasakannan, 2006).

The purpose of this research is to prepare activated carbon from African star apple using seed husks, oil seed and whole seed, treating waste water with activated carbon from Seed husks, Oil seed and Whole seed, in varying quantities and Characterization of activated carbon.

2. Literature review

The activation of the precursor with H₃PO₄ is gaining attention especially for the large-scale manufacturers of ACs because, its environmentally friendly, low energy cost, high carbon yield and ease of recovery (Yagmur et al., 2008). H₃PO₄ acts as an acid catalyst to promote dehydration, bond cleavage, hydrolysis and condensation, accompanied by cross-linking reactions between H₃PO₄ and biopolymers; it also functions as a template because the volume occupied by H₃PO₄ in the interior of the activated precursor is conterminous with the micropore volume of the activated carbon achieved (Vargas et al., 2011). The chemical activation with H₃PO₄ are affected by the experimental conditions of preparation such as carbonization temperature, time of activation, impregnation ratio, acid concentration and heating rate. Research shows that the atmosphere used in the carbonization process has effect on the

physicochemical properties of activated carbon (Mohamed et al., 2010). H₃PO₄ with the maximum ratio of impregnation produces the largest S_{BET} theory, which explains the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of surface area, S_{BET}, ~1792–1819 m²g⁻¹.

Chemical activation of the precursor with Zinc chloride result to the production of ACs with good yield a well-developed porosity in only one step. Impregnation with ZnCl₂ first leads to the material degradation, and on carbonization, produces dehydration that results in charring and aromatization of the carbon skeleton and creation of the pore structure. Furthermore, the precursor is impregnated with a concentrated ZnCl₂ solution during a given contact time, which is followed by evaporation of the solution and, finally, the precursor is carbonized in an inert atmosphere and thoroughly washed to extract the excess of ZnCl₂. The amount of ZnCl₂ impregnated in the precursor and the heat treatment temperature are the variables with direct incidence in the improvement of the porosity. Table 1 shows the Advantages and disadvantages of activation by Chemical Method, however Tables 2–4 shows the Merits and demerits of activation by physical method, Chemical activation of some ACs obtained with ZnCl₂ experimentally using different precursors and Chemical activation of some ACs obtained with H₃PO₄ experimentally using different precursors.

2.1. Adsorption mechanisms

Adsorption is a mass transfer process which involve the gathering of materials at the interface of two phases, for example, gas–solid, gas–liquid, liquid–solid or liquid–liquid interface. The features of the adsorbates and adsorbents are quite detailed and rely upon their constituents. *Physisorption* occur when there is an interaction between the solid surface and the adsorbed molecules by nature. Furthermore, if the attractive forces between adsorbed molecules and the solid surface are due to chemical bonding *chemisorption occur*. Chemisorption occurs only as a monolayer, therefore substance chemisorbed on solid surface are tough to be remove due to stronger forces/bond. Under favourable conditions, Chemisorption and *Physisorption* processes can occur concurrently. Physical adsorption lowers free energy and entropy of the adsorption system, this is an exothermic process (Arami-Niya et al., 2011). For solid–liquid system, adsorption results in the removal of

Table 1
Advantages and disadvantages of activation by chemical method.

Advantages	Disadvantages
ACs are obtained in one step	More expensive
Shorter activation times	Washing stage is required
Lower temperatures of pyrolysis	Inorganic impurities
High control of textural properties	
Thin pore size distributions	
Fully-developed micro porosity	

Table 2
Merits and demerits of activation by physical method.

Merit	Demerit
Prevents the incorporation of contaminants from the ACs.	Obtaining ACs is a two steps process
It is not a corrosive process	Higher temperatures of activation 800–1000 °C
Does not require washing stage.	Poorer control of the porosity
It is relatively cheap	

Table 3Chemical activation of some activated carbons obtained with ZnCl₂ experimentally using different precursors.

Precursor	Ratio of Impregnation (IR)	Temperature of Activation (°C)	Rate of Heating (°C min ⁻¹)	Reference
Almond shell	3	500	–	Vargas et al. (2011)
Coconut shell	2	400	4	Mohamed et al. (2010)
Walnut shells	1	450	5	Yagmur et al. (2008)
Shell from oil palm	–	600	5	Arami-Niya et al., 2011
Licorice residues	1	500	2.5	Tay et al. (2009)
Coffee residue	1	500	5	Mohamed et al. (2010)

Table 4Chemical activation of some ACs obtained with H₃PO₄ experimentally using different precursors.

Precursor	H ₃ PO ₄	Ratio of Impregnation (IR)	Temperature of Activation (°C)	Rate of Heating (°C min ⁻¹)	Reference
Avocado kernel seed	85	6	800	5	Tay et al. (2009)
Jute	30	4	900	20	Bagheri and Abedi, 2009
Pine Wood	90	3	500	–	Mohamed et al. (2010)
Shell from Oil palm	90	0.10	600	15	Arami-Niya et al., 2011
Fruit stone	60	1.02	800	–	Srinivasakannan (2006)
Pecan shell	40	–	500	–	Yagmur et al. (2008)

solutes from solution and their accumulation at solid surface. The remaining solute in the solution attains a dynamic equilibrium with that adsorbed on the solid phase. The quantity of adsorbate that can be taken up by an adsorbent as a function of both concentration and temperature of adsorbate, and the process, when the temperature is constant, can be termed as adsorption isotherm.

When using activated carbon, the adsorption process results from interactions between the carbon surface and the adsorbate which can be electrostatic or non-electrostatic. When the adsorbate is an electrolyte that dissociates in aqueous solution, electrostatic interactions occur; the nature of these interactions may be attractive or repulsive as a result of: (a) charge density of the carbon surface; (b) chemical characteristics of the adsorbate; and (c) ionic strength of the solution. Non-electrostatic interactions are always attractive and can include: (a) -van der Waals forces; (b) hydrophobic interactions; and (c) hydrogen bonding. According to (Tay et al., 2009), the properties of the adsorbate that mainly influence the adsorption process in AC are: (a) molecular size; (b) solubility; and (c) nature of the substituents (in the case of aromatic adsorbates). The molecular size determines the accessibility of the adsorbate to the pores of the carbon, the solubility determines the degree of hydrophobic interactions between the adsorbate and the carbon surface. When the adsorbate is aromatic, the substituents of the aromatic ring have the ability to withdraw or release electrons, which therefore affects the non-electrostatic interactions between the adsorbate and the activated carbon surface.

3. Methods

Ripe African star apple (Agbalumo), from an open major market in Oju-ore, Ogun state, Nigeria and Industrial wastewater from Doyin Investment Limited, Okokomaiko, Lagos State, Nigeria, were used for this study. Distilled water was generated from chemical Engineering laboratory, Covenant University, Ota. H₃PO₄ and ZnCl₂ were of J.T Baker Grade NJ08865 USA.

Electronic weighing balance, 250 mL Conical flask, measuring cylinders 250 mL, 500 mL, and 1,000 mL each, 200 and 500 mL Beaker, Mechanical Shaker, Microwave Oven, Drying Oven, Plastic transparent containers for samples, Thermo Scientific Thermolyne A1 Premium Muffle Furnace - 208V from USA, Thermometer, Mortar, Pestle, Funnel, Cotton Wool, Spatula, stopwatch, Mortar pestle, Funnel, Cotton wool, Spatula, stopwatch and scanning electroscopie Microscope (SEM) model FEI-QUANTA 200. The

characteristics of waste water used in this study are pH, Temperature (°C), TDS (mg/L), TSS (mg/L) and BOD (mg/L).

3.1. Preparation of activated carbon

The first set of experiment involves the preparation of activated carbon from African star apple seed husks, oil seeds and whole seed using zinc chloride (ZnCl₂) and phosphoric acid H₃PO₄. A stainless steel vertical reactor was placed on a table; 10 g of the precursor was weighed and poured into it. The weighed precursor was carbonized at a temperature of 500 °C for 2 h in a furnace. An aqueous solution of 100 mL in 80 wt% concentration of phosphoric acid and zinc chloride was used respectively. The char produced was added with the aqueous solution of phosphoric acid and zinc chloride individually. After 1 h of proper mixing, the apparatus was allowed to cool; oven was switched on and set up at 105 °C. The blend got dried out in an oven at a temperature of 105 °C for 2 h. After which the activated product was then cooled at room temperature and washed with warm distilled water until it reached a pH of 7 to remove any undiluted residue of phosphoric acid and zinc chloride respectively. This preparation procedure was done for 20 g, 30 g, 40 g and 50 g of the African star apple seed husks, oil seeds and whole seed precursors. Finally, the dried antecedent was ground and sieved to get the molecule size of 125–150 μm. All proximate analysis was carried on the activated carbon. It was stored in glassware's for further use. The results were tabulated.

3.2. Industrial wastewater treatment

The second set of experiment involves the treatment of Industrial wastewater using African star apple seed husks, oil seeds and whole seed using zinc chloride (ZnCl₂) and phosphoric acid H₃PO₄. 1 L of wastewater samples was measured and placed on a table. 200 mL of industrial wastewater was weighed out. 10 g of phosphoric acid and zinc chloride, African star apple seed husks, oil seeds and whole seed activated carbon was weighed individually and mixed with the 200 mL wastewater sample. The mixture was poured into a conical flask. A warm plate magnetic stirrer was turned on and set to a temperature of 30 °C before the mixture was placed on it and then shaken for 30 min at 20 rev/s. Whatman No 42 filter paper was place in a glass funnel before the samples was filtered having a fine porosity and molecule maintenance of 2.5 μm. The same treatment process was done for 60 min, 90 min, 120 min and 150 min of the

same activated carbon. Analysis was done on each of the filtered liquid with respect to the suspended and dissolved particles. 3 g of each sample of the bio adsorbents was weighed and placed in a furnace heated at a temperature of 105 °C for Moisture content and Bulk density, and 700 °C for Ash content characterization respectively. These processes were done in 1 h after heating, the heated samples were covered with a lid and weighed quickly.

Temperature, pH, TSS, TDS and BOD of the treated water with varying contact time was investigated using standard methods and equipment in correlation with Federal Environmental Protection Agency (FEPA) standard value of water.

4. Results

4.1. Effect of activating agent on yield

The activated carbon yields were obtained following the conditions of preparation. $ZnCl_2$ and H_3PO_4 were used as the activating agents activated using 15 wt% and 80 wt% respectively and a common carbonization temperature of 500 °C. From Fig. 1, it is shown that the ZSHAC had the highest yield of 75.2% after been activated with the same concentration and carbonized at the same temperature with ZOSAC AND ZWSAC having 72.2% and 69.9% respectively. Zinc chloride acting as a dehydrating agent fosters the H_2 and O_2 to leave as (H_2O) leaving behind the carbon atoms better in the ZSHAC than the ZOSAC and ZWSAC because of the oil content in each of these. The yield of the phosphoric acid impregnated samples was very close to that of the zinc chloride impregnated sample simply because the phosphoric acid also has a similar dehydrating effect on the precursor that promotes the carbonization yield and removal of hydrogen and oxygen as water. Furthermore, as observed from Fig. 1, the yield of the PSHAC was 55.3% which is higher than 54.3% and 41.6% of the POSAC and POWSAC respectively which did not meet the expected value because the other conditions like the carbonization temperature(500 °C) and concentration of the phosphoric acid (80 wt%) were not exactly favourable.

4.2. Scanning electron microscopy (SEM) micrograph

From the micrographs of the zinc chloride impregnated samples, it was seen that Fig. 2a ZSHAC, Fig. 2b. ZOSAC, and Fig. 2c. ZWSAC are rough, with protrusions quite prevalent in the biomass and illuminations dotted in the matrix appears to be dark field. High level of porosity was observed on the external surface of the ZSHAC, ZOSAC, and ZWSAC. With ZSHAC relatively more porous than ZOSAC and ZWSAC. Furthermore, higher levels of blunted sponge-like protrusions (Kang, 2013) were observed in ZSHAC when compared to ZOSAC and ZWSAC which might be a probable reason for better trapping and adsorption performance. Also from

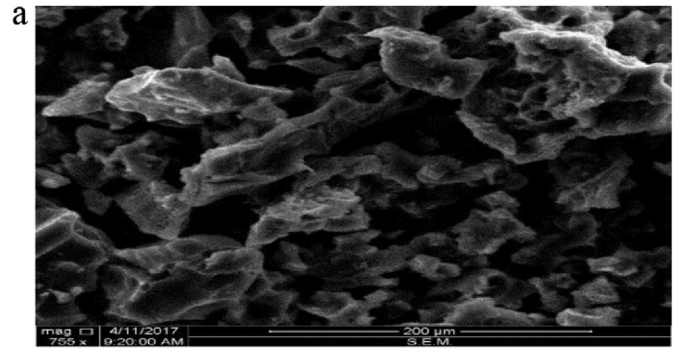


Fig. 2a. ZSHAC SEM image.

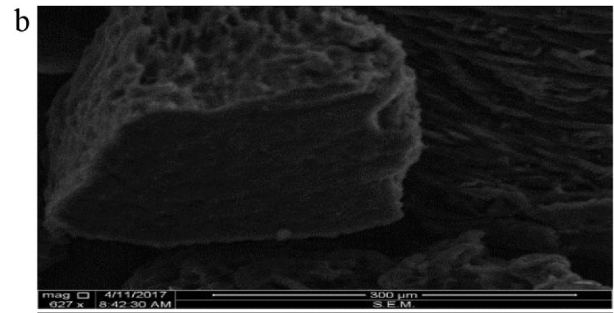


Fig. 2b. ZOSAC SEM image.

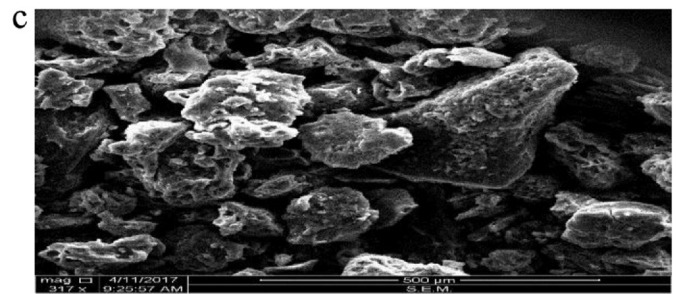


Fig. 2c. ZWSAC SEM image.

the micrographs of the phosphoric acid impregnated samples shown in Fig. 2e, shows that POSAC is relatively more porous than PSHAC and PWSAC which are Fig. 2d and f respectively, making it a better adsorption performer of the suspended and dissolved particles.

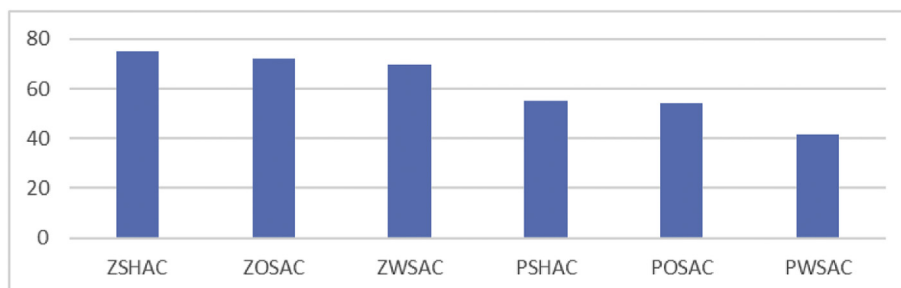


Fig. 1. Activated carbon Yields.

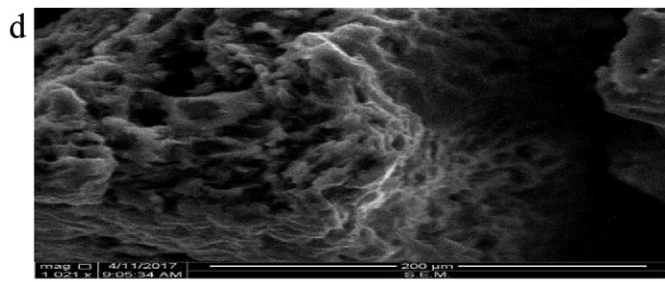


Fig. 2d. PSHAC SEM image.

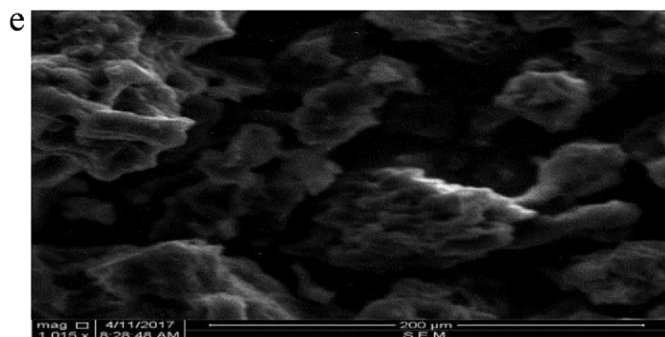


Fig. 2e. POSAC SEM image.

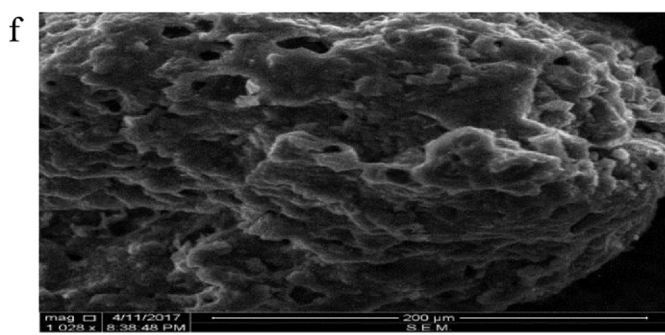


Fig. 2f. PWSAC SEM image.

4.3. Fourier transformed infrared (FT-IR) spectroscopy

Figs. 3a to 8b shows the FT-IR spectrum. From the region of the transmittance peaks and notional structure of the ZSHAC, ZOSAC, ZWSAC, PSHAC, POSAC and PWSAC, it was possible to assign some of the functional groups. The FTIR spectrum of ZSHAC as shown in the figure above showed distinct peaks at 2,203.84 (C-H aldehydes), 1,565.32 (C=C stretching), ZOSAC showing 2,284.19 (C-H aldehydes), 2,195.52–1,978.38 (C≡C stretch shift), 1,567.68 (C=C stretching), 1,086.27 (C-N stretch), 868.75–582.54 (C-C stretching). ZWSAC also showing distinct peaks of 3,271.89 (O-H stretching), 2,919.23(C-H stretch shift), 2,323.01–2,169.53 (C≡C stretch shift), 1,574.42 (C=C stretching), 1,390.95 (C-H asymmetrical stretch), 1,240.40 (C-O asymmetrical stretch), 876.69–522.21(C-C stretching). PSHAC showing 2,576.59 (C-H aldehydes), 2,334.59–1,975.43 (C≡C stretch shift), 1,688.64–1,586.78 (C=C stretching), 1153.42 (C-N stretch), 873.08–592.82 (C-C stretching). Noted was the likelihood of presence of fragrant rings from the pinnacles seen in the vicinity of 1,560 and 1,700 cm^{-1} ; however, N-H holding, for instance, from -NH_2 and NH_3 moieties, has an ingestion band in this

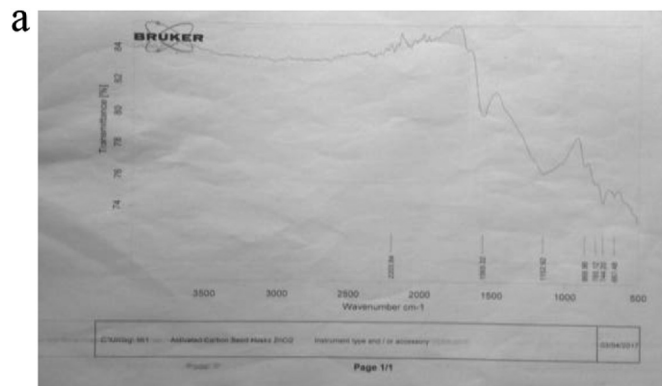


Fig. 3a. Unused ZSHAC.

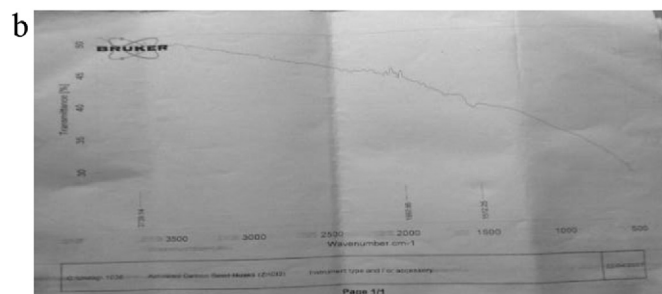


Fig. 3b. Used ZSHAC.

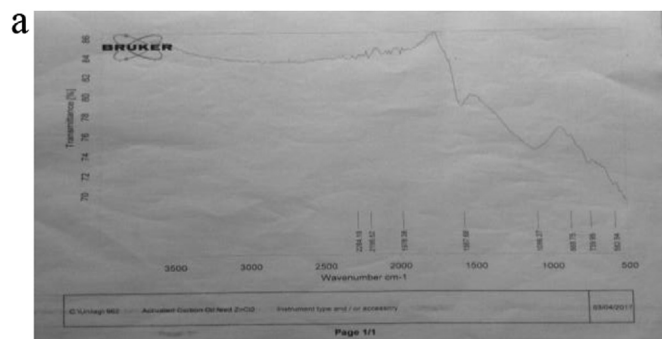


Fig. 4a. Unused ZOSAC.

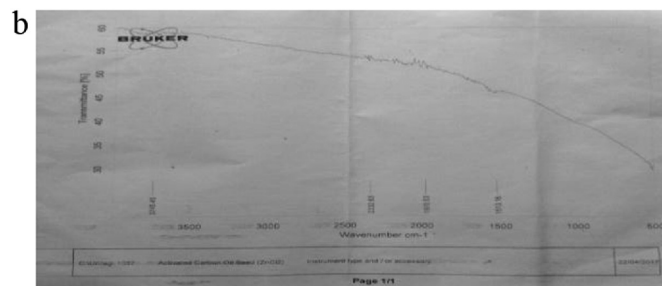


Fig. 4b. Used ZOSAC.

district. Likewise, the extending frequencies of N-H bonds could likewise be mistaken for those of O-H frequencies in the 3,200 and 3,700 cm^{-1} area. The FTIR results of activated carbon and used adsorbents as shown in the figures above shows that some peaks

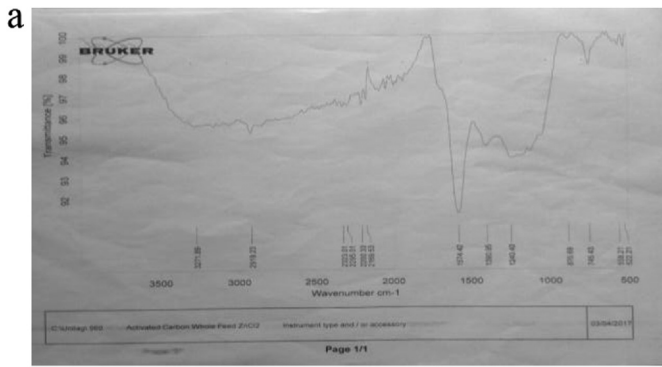


Fig. 5a. Unused ZWSAC.

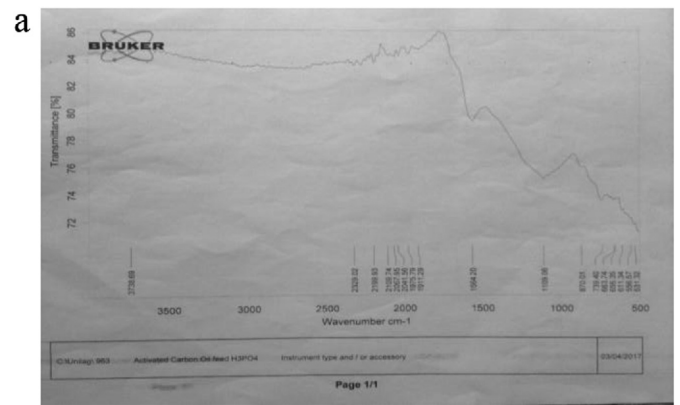


Fig. 7a. Unused POSAC.

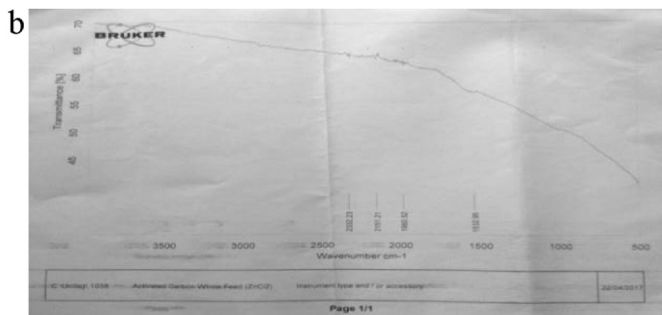


Fig. 5b. Used ZWSAC.

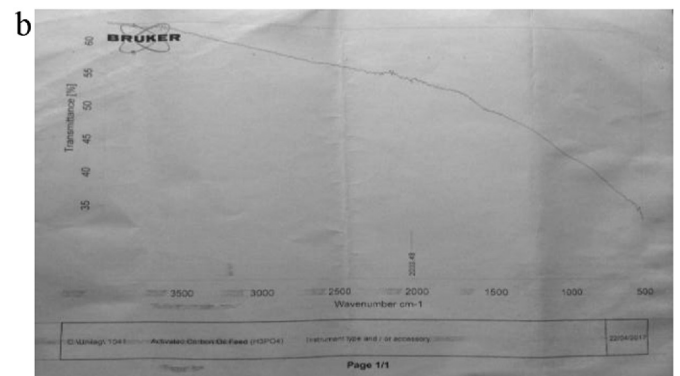


Fig. 7b. Used POSAC.

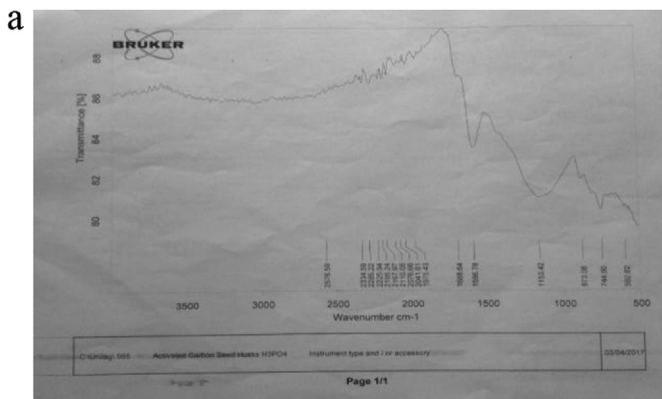


Fig. 6a. Unused PSHAC.

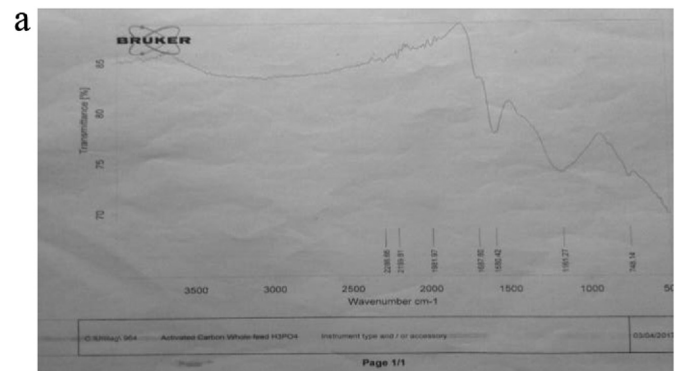


Fig. 8a. Unused PWSAC.

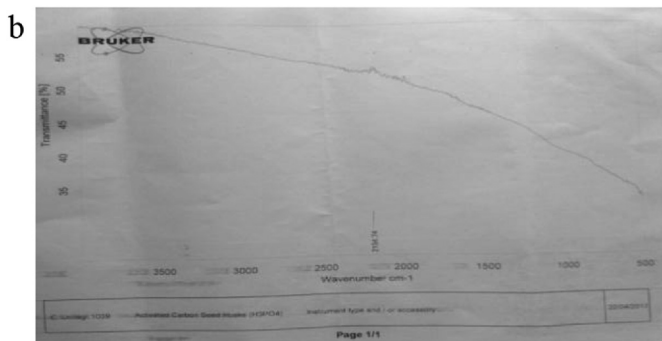


Fig. 6b. Used PSHAC.

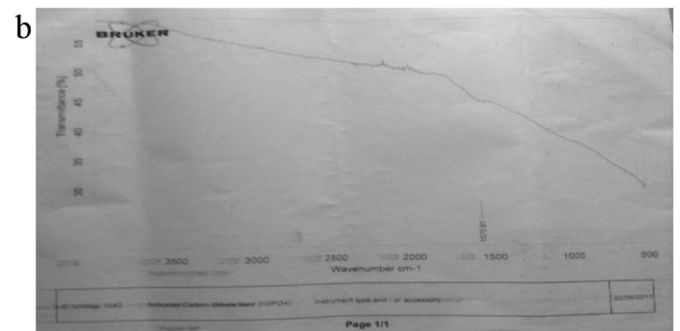


Fig. 8b. Used PWSAC.

Table 5
Investigation on treated wastewater.

Properties	FEPA Limits	In-situ Wastewater
pH	6–9	7.89
Temperature (°C)	25–30	28.9
Total Dissolved Solid (mg/L)	2000	814.11
Total Suspended solid (mg/L)	15–30	303.91
Biochemical Oxygen Demand (mg/L)	10–50	35.87

were shifted, and that new peaks were also noticed. Changes noticed in the spectra signifies interactive effects due to involvement of those functional groups during production and use of the adsorbents. The changes seen in the peaks of the adsorbents after usage could be resolved to be the direct result of adsorptive uptake of suspended and dissolved particles from the wastewater by the adsorbents. The different number of absorption peaks demonstrated by the samples reflected the complex nature of these materials (El-Khaiary, 2008). Table 5 compares the properties of the wastewater according to (FEPA) standards.

4.4. Effect on contact time on pH, temperature, TDS, TSS and BOD

As shown in Fig. 9, the pH decrease as contact time of the activated carbon with wastewater increases as shown in the plots of pH above. With ZSHAC at 30 min having a pH of 7.65 shows that it reduced the in-situ wastewater pH of 7.89, 7.07 at 120 min and 7.01 at 150 min shows that contact time with the wastewater reduced the pH at 30 min but further decreasing it with increase in contact time. It is seen from the plots above that there was a great difference in the pH at 90 min and 120 min having 7.42 and 7.07. The ZSHAC had a better pH of 7.01 in line with the Federal Protection and Environmental Agency (FEPA) limit of treated wastewater pH of 6–9 than that of the ZOSAC and ZWSAC with ZOSAC having 7.80 at 30 min, 7.07 at 120 min and 6.86 at 150 min and ZWSAC having 7.87 at 30 min, 7.11 at 120 min and 6.96 at 150 min. It was also seen that the pH started having steady values at 12033 min

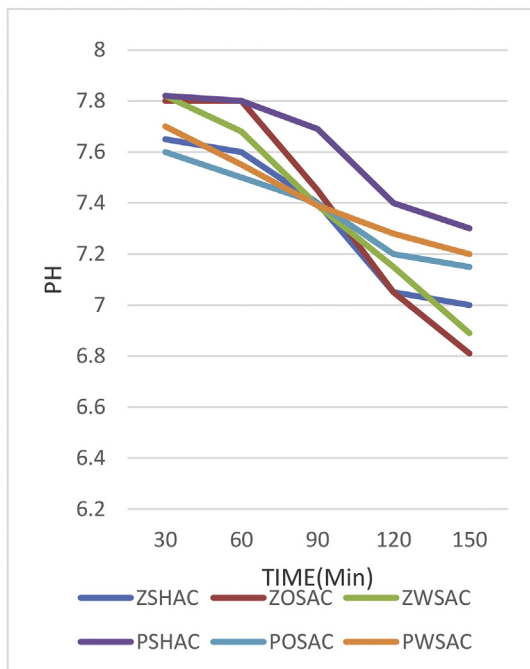


Fig. 9. Effect of contact time on pH.

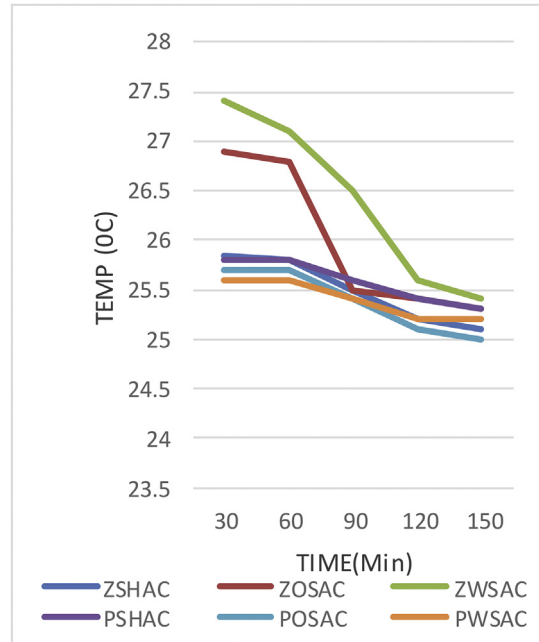


Fig. 10. Effect of contact time on temperature.

and 150 min indicating that further increase in the contact time might not necessarily decrease the pH (Yeddou N, 2005). Fig. 10 explained further that, temperature decrease as contact time of the activated carbon with wastewater increases as shown in the plot of temperatures above. With ZSHAC at 30 min shows that it reduced the in-situ wastewater temperature of 26.9 having temperature of 25.9, 25.8 at 60 min, 25.5 at 90 min, 25.2 at 120 min and

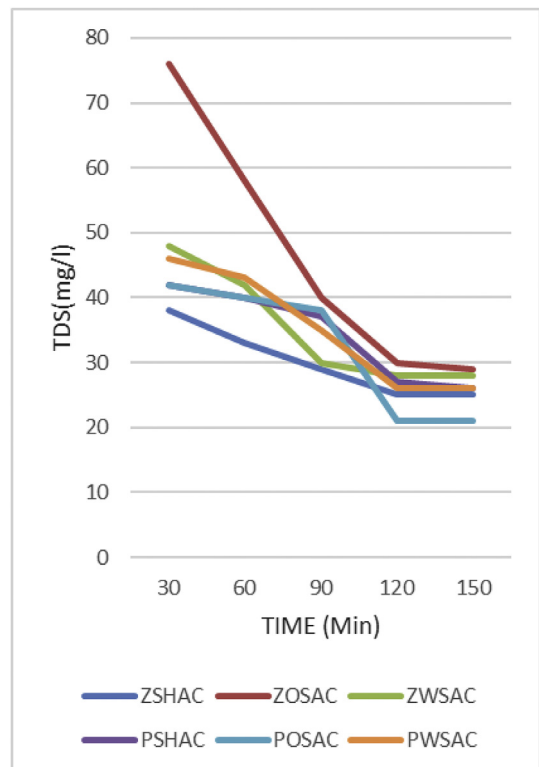


Fig. 11. Effect of contact time on TDS.

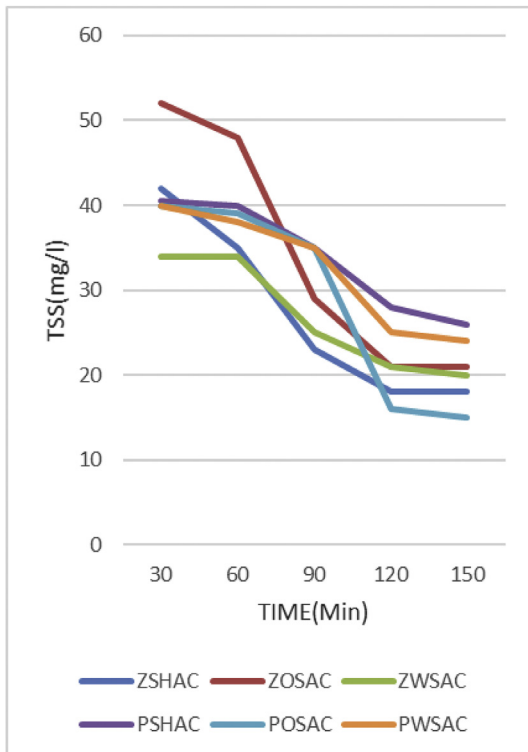


Fig. 12. Effect of contact time on TSS.

25.1 at 150 min shows that temperature decreased steadily at the increasing time. It is also seen that at 120 min and 150 min, the value of the pH and temperature did not vary much difference indicating that further increase in the contact time will result in constant temperature (Janhom, 2009). The ZSHAC had a better temperature correlating with the FEPA limit of treated wastewater temperature of 25–30 °C than that of the ZOSAC and ZWSAC. As seen in the plot of TDS above in Fig. 11, increase in contact time of the activated carbon with wastewater, result to decrease in TDS. Having considered the FEPA limits for TDS of 2000 mg/l, ZSHAC had a very good adsorption performance with increase in the contact time on the removal of TDS with 38.53 at 30 min shows that it reduced the in-situ wastewater TDS of 814.11, and 33.14 at 60 min, 28.98 at 90 min, 24.81 at 120 min, and 24.20 at 150 min showing no

big difference in TDS removal at different time. Although the ZOSAC and ZWSAC also had values between the FEPA limits of 15–30 mg/L but ZSHAC had better performance. In Fig. 12, the TSS above, that increase in contact time of the activated carbon with wastewater, decreases the TSS. Having considered the FEPA limits for TSS of 15–30 mg/L, ZSHAC had a very good adsorption performance with increase in the contact time on the removal of TSS with 42.09 at 30 min shows that it reduced the in-situ wastewater TSS of 303.91, 35.11 at 60 min, 22.78 at 90min, 17.97 at 120 min, and 17.64 at 150 min showing the great effect of the contact time in the decreasing of TSS between 30 and 120 min and becoming relatively constant between 120 and 150 min. With the BOD been used as the gauge of the effectiveness of wastewater treatment, it is seen from the graph of BOD against contact time above that increase in contact time of the activated carbon with wastewater, decreases the BOD level in the wastewater. At 30 min, there was BOD removal for all the zinc chloride activated carbon but at 120 min and 150 min, BOD removal was more significant. ZSHAC at these various times had the best BOD removal compared to ZOSAC and ZWSAC. All the zinc chloride activated carbon are in line with the FEPA limits for BOD of 10–50 mg/L. Also from these, it shows that ZWSAC is also a better performer than ZOSAC comparing the values at different times (Menkiti, 2011). Fig. 13 shows the effect of contact time on pH.

4.5. Physicochemical properties of activated carbon

From Fig. 14, POSAC is seen to have higher moisture content than that of PSHAC and PWSAC. This is because the POSAC has a larger pore volume and better structured porosity than that of the PSHAC and PWSAC. The larger pore volume is as a result of the presence of the H_3PO_4 in the interior of the particles during the carbonization process, inhibiting the contraction of the pore volume caused by the heat of carbonization. ZSHAC is seen to also have higher moisture content than the ZOSAC and ZWSAC. This is because the ZSHAC has a larger pore volume and better structured porosity than that of the ZOSAC and ZWSAC. Therefore, moisture content of the activated carbon has a relationship with pore volume and porosity. Fig. 15 shows that POSAC is seen to have higher ash content than that of PSHAC and PWSAC. This is because the phosphate compounds formed by phosphoric acid activating agent used in the production of the POSAC has added to the inorganic matter in the activated carbon. Therefore, increasing the amount of non-ignitable residue left in the POSAC than PSHAC and PWSAC after the activated carbon is burnt. ZSHAC is seen to also have higher ash content than the ZOSAC and ZWSAC.

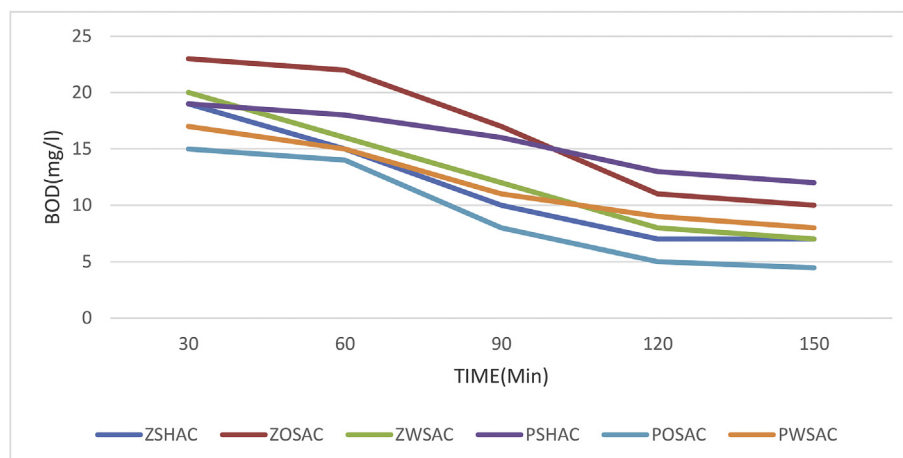


Fig. 13. Effect of contact time on BOD.

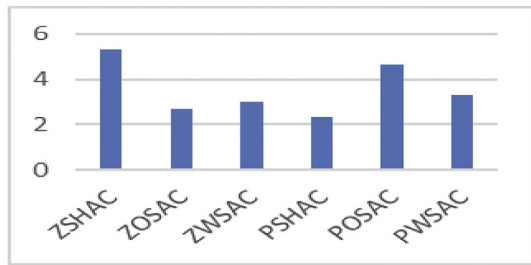


Fig. 14. Moisture content of activated carbon.

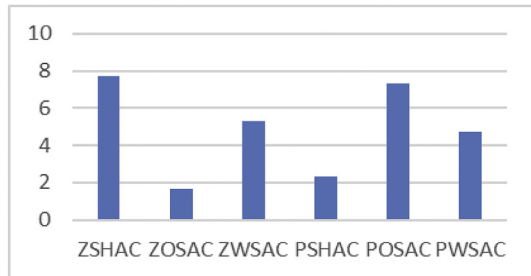


Fig. 15. Ash content of activated carbon.

5. Conclusion

African star apple whole seed, seed husks and oil seed are effective precursors for activated carbon production. $ZnCl_2$ and H_3PO_4 are good activating agents as they produced activated carbon with high adsorption performance from the seed husks and oil seed respectively. Seed husks of zinc chloride produced an activated carbon with the highest adsorptive performance for pH, temperature, TDS, TSS and BOD removal. Oil seeds of phosphoric acid produced an activated carbon with the highest adsorptive performance for pH, temperature, TDS, TSS and BOD removal. Increasing the contact time also, of the activated carbon with wastewater causes a steady decrease in the pH, Temperature, TDS, TSS and BOD of the wastewater. The limitation of this study is that the fruits are seasonal, and adequate fruits will be made available for future research plan specifically for wastewater treatment.

Funding information

This research is partially sponsored by Covenant University.

APPENDIX A

Table 1
Results showing Yield Determination, Moisture content, Ash Content and Bulk Density

Sample	Activating agent	$W_o(g)$	$W_c(g)$	Yield %	$W_o(g)$	$W_c(g)$	Moisture content (%)	$W_o(g)$	$W_c(g)$	Ash content	M(g)	V(cm^3)	Bulk density g/cm^3
ZSHAC	$ZnCl_2$	391	294.1	75.2	3.0	2.84	5.33	3.0	0.23	7.7	50.0	75.0	0.67
ZOSAC	$ZnCl_2$	214	154.6	72.2	3.0	2.92	2.67	3.0	0.05	1.7	50.0	100.0	0.50
ZWSAC	$ZnCl_2$	373	260.8	69.9	3.0	2.91	3.00	3.0	0.16	5.3	50.0	90.0	0.56
PSHAC	H_3PO_4	380	210.3	55.3	3.0	2.93	2.33	3.0	0.07	2.3	50.0	70.0	0.71
POSAC	H_3PO_4	214	116.1	54.3	3.0	2.86	4.67	3.0	0.22	7.3	50.0	90.0	0.56
PWSAC	H_3PO_4	400	166.5	41.6	3.0	2.90	3.33	3.0	0.14	4.7	50.0	78.0	0.64

APPENDIX B. INVESTIGATION OF TREATED WASTEWATER

Table 2
Effect of contact time on PSHAC treated wastewater

Time(min)	pH	Temperature($^{\circ}C$)	TDS(mg/L)	TSS(mg/L)	BOD(mg/L)
30	7.83	25.8	41.58	40.92	19.4
60	7.80	25.8	40.5	39.87	17.8
90	7.68	25.6	37.56	34.64	15.6
120	7.39	25.4	28.47	27.9	12.7
150	7.31	25.3	27.32	26.0	11.9

Table 3
Effect of contact time on POSAC treated wastewater

Time(min)	pH	Temperature($^{\circ}C$)	TDS(mg/L)	TSS(mg/L)	BOD(mg/L)
30	7.6	25.7	41.94	41.11	15.1
60	7.49	25.7	39.89	39.09	13.5
90	7.39	25.4	37.35	34.40	8.2
120	7.2	25.1	21.17	16.61	5.2
150	7.14	25.0	21.09	15.4	4.8

Table 4
Effect of contact time on PWSAC treated wastewater

Time(min)	pH	Temperature($^{\circ}C$)	TDS(mg/L)	TSS(mg/L)	BOD(mg/L)
30	7.69	25.6	46.32	40.22	17.2
60	7.54	25.6	42.5	38.17	14.9
90	7.38	25.4	35.95	34.63	11.0
120	7.27	25.2	27.44	24.8	9.6
150	7.2	25.2	27.13	23.3	8.8

Table 5
Effect of contact time on ZSHAC treated wastewater

Time(min)	pH	Temperature($^{\circ}C$)	TDS(mg/L)	TSS(mg/L)	BOD(mg/L)
30	7.65	25.9	38.53	42.09	19
60	7.59	25.8	33.14	35.11	15
90	7.42	25.5	28.98	22.78	10.4
120	7.07	25.2	24.81	17.97	7.7
150	7.01	25.1	24.20	17.64	6.28

Table 6
Effect of contact time on ZOSAC treated wastewater

Time(min)	pH	Temperature(°C)	TDS(mg/L)	TSS(mg/L)	BOD(mg/L)
30	7.80	26.9	74.9	53.6	23.56
60	7.79	26.8	56.71	47.46	21.4
90	7.48	25.5	39.42	28.40	17.23
120	7.07	25.5	30.14	22.19	11.12
150	6.86	25.3	38.86	22.07	10.49

Table 7
Effect of contact time on ZWSAC treated wastewater.

Time(min)	pH	Temperature(°C)	TDS(mg/L)	TSS(mg/L)	BOD(mg/L)
30	7.87	27.4	47.85	34.05	20.12
60	7.72	27.1	42.44	33.71	16.66
90	7.37	26.5	30.8	25.28	12.04
120	7.11	25.6	27.67	21.09	8.29
150	6.96	25.3	27.65	20.81	7.36

Appendix C. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2019.05.378>.

References

- Arami-Niya, A., Daud, W., Mjalli, F.S., 2011. Comparative study of the textural characteristics of oil palm shell activated carbon produced by chemical and physical activation for methane adsorption. *Chem. Eng. Res. Des.* 89, 657–664.
- Ahmedna, M., Marshall, W.E., Rao, R.M., 2000. Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. *Bioresour. Technol.* 71, 113–123.
- Bagheri, N., Abedi, J., 2009. Preparation of high surface area activated carbon from corn by chemical activation using potassium hydroxide. *Chem. Eng. Res. Des.* 87, 1059–1064.
- Bansal, E.A., 1988. Active carbon. *J. Dispersion Sci. Technol.* 76, 657–664.
- El-Khaiary, H.A., 2008. Properties and Process of Carbon Activation. Hassan Press, Abu Dhabi.
- Janhom, T.W.S., 2009. Characterization of brewery wastewater with spectrofluorometry analysis. *J. Environ. Mgt.* 55, 1184–1190.
- Kang, P.M., 2013. Surface chemistry and adsorption mechanism of cadmium ion on activated carbon derived from *Garcinia mangostana* shell. *J. Food Prod. Mark.* 22, 471–485.
- Mattson, E.A., 1971. Activated carbon: surface chemistry and adsorption from solution. *Resour. Conserv. Recycl.* 52, 13–27.
- Menkiti, M.C., 2011. Bioadsorption of suspended and dissolved particles from coal washery effluent onto fluted pumpkin seed shell biomass. *J. Porous Mater.* 9, 15–18.
- Mohamed, A.R., Mohammadi, M., Darzi, G.N., 2010. Preparation of carbon molecular sieve from lignocellulosic biomass: a review. *Renew. Sustain. Energy Rev.* 14, 1591–1599.
- Mohammadi, S.Z., Karimi, M.A., Afzali, D., Mansouri, F., 2010. Removal of Pb(II) from aqueous solutions using activated carbon from Sea-buckthorn stones by chemical activation. *Desalination* 262, 86–93.
- Namasivayam, C., Kadirvelu, K., 1997. Activated carbons prepared from coir pith by physical and chemical activation methods. *Bioresour. Technol.* 62, 123–127.
- Olivares-Marín, M., Fernández-González, C., Macías-García, A., Gómez-Serrano, V., 2006. Preparation of activated carbon from cherry stones by chemical activation with ZnCl₂. *Appl. Surf. Sci.* 252, 5967–5971.
- Phan, N.H., Rio, S., Faur, C., Le Coq, L., Le Cloirec, P., Nguyen, T.H., 2006. Production of fibrous activated carbons from natural cellulose (jute, coconut) fibers for water treatment applications. *Carbon* 44, 2569–2577.
- Song, C., Libo, Z., Hongying, X., Shengzhou, Z., Jinhui, P., Shixing, W., 2016. Crofton weed derived activated carbon by microwave-induced KOH activation and application to wastewater treatment. *J. Porous Mater.* 23, 1597–1607.
- Srinivasakannan, C., 2006. Production of activated carbon from rubber wood sawdust. *Biomass Bioenergy* 9, 234–235.
- Tay, T., Ucar, S., Karagöz, S., 2009. Preparation and characterization of activated carbon from waste biomass. *J. Hazard Mater.* 165, 1–3.
- Vargas, A.M.M., Cazetta, A.L., Garcia, C.A., Moraes, J.C.G., Nogami, E.M., Lenzi, E., Costa, W.F., Almeida, V.C., 2011. Preparation and characterization of activated carbon from a new raw lignocellulosic material: flamboyant (*Delonix regia*) pods. *J. Environ. Manag.* 92, 3301–4797.
- Yagmur, E., Ozmak, M., Aktas, Z., 2008. A novel method for production of activated carbon from waste tea by chemical activation with microwave energy. *Fuel* 87, 3278–3285.
- Yeddou N, B.A., 2005. Kinetic models for the sorption of dye from aqueous solution by clay-wood sawdust mixtu. *Carbon* 64, 499–508.