

International Journal of Advances in Scientific Research and Engineering (ijasre)

E-ISSN: 2454-8006

DOI: http://dx.doi.org/10.7324/IJASRE.2018.32615

Volume 4, Issue 2 February-2018

The Promising Precursors for Development of Activated Carbon: Agricultural Waste Materials - A Review

Luka Y.¹, Highina, B. K.² and Zubairu, A.³

¹Department of Chemical Engineering,

Modibbo Adama University of Technology,

Yola, Adamawa State, Nigeria

^{2,3}Department of Chemical Engineering,

University of Maiduguri, Borno State,

Nigeria

ABSTRACT

This paper contains a review on agricultural waste materials as promising precursors for development of activated carbon. The phenomenon behind higher adsorptive capacity of activated carbon or activated charcoal also known as solid sponge was mentioned. The composition and structure of activated carbon were also discussed. The agricultural waste materials availability, renewability, pollution control and economic benefit for activated carbon development were presented. The review also explained Steps involved in development of activated carbon, Characterization and Properties of activated carbon as well as Applications of activated carbon and Contactors used.

Keywords: Activated carbon, Agricultural waste, Development, Applications and contactors.

1. INTRODUCTION

Foo and Lee [1] described activated carbon as one of the most popular adsorbents used in industries for the removal of organic and inorganic compounds from gaseous and liquid streams. According to a group of researchers activated carbon is referred to as a carbonaceous material that can be prepared by the pyrolysis of many inexpensive materials that have a high carbon content and low inorganic content. They stated that on a commercial scale, activated carbon is prepared by the pyrolysis and activation of high-cost starting materials, such as wood, petroleum and coal, making it expensive and unjustified as a process of pollution control [2].Presently, there are many researches on the development of adsorbents, using waste materials that can substitute or replace the commercial available ones which are very expensive compare with the one obtained from biomaterials such as agricultural materials [3; 4; 5; 6]. Furthermore, several reviews report some researched work done and their applications (agricultural materials) for the removal of specific pollutants from aqueous and gaseous phases, which include heavy metals, dye, formaldehyde and carbon dioxide capture [7; 8; 9]. Activated carbon is known as a carbonaceous material showing a well-developed surface area and porous texture. Industrial, agricultural and domestic activities are the major source of water pollution due to chemicals which contain heavy metals, hazardous waste which can affect health and environment [10].

Adsorption is a mechanism in which an adsorbate (compound), in gas or liquid phase, accumulates on a solid surface (adsorbent). It is based on the capability of porous materials with large surfaces to selectively retain compounds on the surface of the solid. Adsorption process can be classified into two namely: physical and chemical adsorptions. Physical adsorption is attained by Van der Waals forces, dipole interactions, and hydrogen binding. Electron exchange is not involved between adsorbent and adsorbate. Due to the fact that there is no activation energy required for physical adsorption, the time needed to reach equilibrium is very short. Physical adsorption is a non–specific and a reversible process. Whereas Chemical adsorption is achieved as results of the

chemical link between adsorbent and adsorbate molecule, hence it is specific and irreversible as well as the chemical or electronic properties of adsorbent are changed. Binding between adsorbent and adsorbate by covalent bond is called weak chemical adsorption, and that by ionic bonds is called strong chemical adsorption [11].

Adsorption process is being widely used by various researchers for removal of heavy metals from waste streams and activated carbon has been frequently used as an adsorbent and in catalysis or separation processes [10; 12; 13; 14]. The first quantitative studies on adsorption were carried out in 1773 by C. W. Scheele on the uptake of gases by charcoal and clays. Later, Lowitz used charcoal to decolorized tartaric acid solution which was successfully achieved. In addition, Larvitz in1792 and Kehl in 1793 noticed similar phenomena with vegetable and animal charcoal, respectively. The words adsorption was proposed by Bois-Reymond and introduced into literature by Kayser in 1881. This was the beginning of using adsorption process for the removal of solutes from solutions and gases from atmosphere. Nevertheless, the credit of development of commercial activated carbon goes to Raphael Von Ostrejko whose inventions were patented in 1900 and 1901 [15; 16].

Adsorption is a superficial phenomenon, as high surface area the activated carbon or activated charcoal also known as solid sponge could attain implies higher adsorptive capacity it will have. The surface is a significant characteristic of the activated carbon which has a typical range of $500 - 1000 m^2/g$. In general, the high adsorptive capacities of activated carbons are highly related to porous characteristics such as surface area, pore volume and pore size distribution and the presence of functional groups on pore surfaces play a significant role in the adsorptive capacities of activated carbons. The porous structure of activated carbons contain up to 15 % of mineral matter in the form of ash content [13]. A pore is a type of cavity which is linked to the surface of a solid and allows the connection of fluids into, out of, or through a material [17]. Activated carbons with abundance of micropores are extensively used for adsorption of small molecule pollutants, and highly developed mesoporous activated carbons are used for the adsorption of larger molecules such as dyes [13; 18]. Aznar [17] stated that Macropores are the big size pores and cannot be filled by capillary condensation. The researcher further explained that one of the main functions of the macroporous is to ensure that the adsorbate arrives quickly to the smaller size pores located deeper in the activated carbon. Nevertheless, macropores can also retain big molecules such as humic acids, which are generated in decomposition of organic matter. According to [16] the porous structure is one of the main physical property that characterizes activated carbons and can be classified into three major groups namely: micropores with a pore width of less than $2.0 \times 10^{-9} m$, mesopores with widths from $2.0 to 50.0 \times 10^{-9} m$ and macropores with a pore width larger than $50.0 \times 10^{-9} m$ [16; 17; 19] as shown in Figure 1.

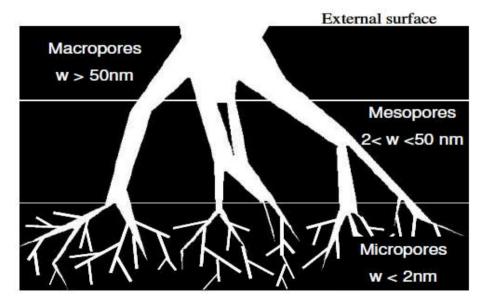


Figure 1: Depicting Schematic Representation of the Pore Network of a Carbon Adsorbent [16; 17].

The purpose of this review is to throw more light on agricultural waste materials as the promising precursors for development of activated carbon and the objectives will be achieved by understanding: the composition and structure of materials required for development of activated carbon, agricultural waste materials for activated carbon, Steps involved in development of activated carbon, Characterization and Properties of activated carbon, Applications and Contactors used for activated carbon.

2. COMPOSITION AND STRUCTURE OF ACTIVATED CARBON

The composition of Carbon materials are mainly the element carbon. Due to its atomic structure $(1s^2, 2s^2, 2p^2)$ the element has unique bonding abilities, both with other elements and with itself. Depending on the nature of hybridization involved they are able to bond with other carbon atoms, giving rise to three major allotropic forms of carbon namely; diamond, graphite and fullerenes

[16]. Activated carbon is a black solid substance, amorphous, microcrystalline, a non-graphite form of carbon and tasteless [20; 21], which implies it cannot be converted into crystalline graphite even at temperature above 3000 °C [21]. According to [11] during carbonization of the precursors in the process of development of activated carbon, the free elementary carbon atoms self-assemble to form elementary graphite crystallites which are made up of 3 to 4 parallel hexagonal carbon ring layers. The main structure of activated carbon is composed of microcrystalline (amorphous) graphitic-like sheets, known as basal planes, which are randomly cross-linked and surrounded by a number of unpaired electrons. These particular architectural features make activated carbon enormously porous and useful for applications in catalysis and adsorption with a wide range of molecules. The arrangement of carbon atoms in graphite and activated carbon are shown in Figure 2.

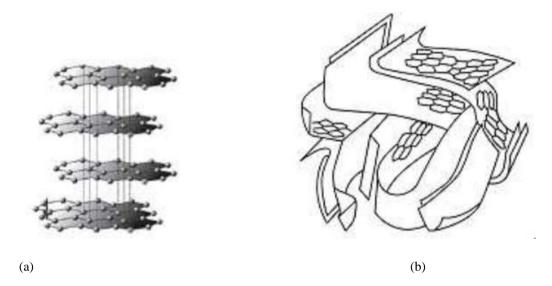


Figure 2: Arrangement of Carbon Atoms: (a) Graphite Crystal; (b) Microstructure Activated Carbon [11].

Activated carbon cannot be characterized by any distinctive chemical formula .Based on its physical characteristic; activated carbon can be classified into several groups which include: powdered activated carbon, granulated activated carbon, extracted activated carbon, activated carbon monoliths, pellet activated carbon, fibrous activated carbon and activated carbon cloths [21; 22].Activated carbon is associated with heteroatoms like oxygen, sulfur, hydrogen, nitrogen, halogen and other elements in the forms of functional groups and/or atoms which bonded chemically to the structure. Oxygen is one of the predominant atoms which exist in the form of functional groups such as carboxyl, carbonyl, phenols and lactone. The precursor and the activation treatment will determine the nature and amount of oxygen surface group that will be contained in any activated carbon. These carbon–oxygen groups of acidic (carboxylic, lactonic) evolve as CO_2 where as that of non-acidic (carbonyl, ether, quinone) are given out as CO, upon thermal decomposition. Meanwhile, phenol groups also evolve as CO, similar to those non-acidic, while anhydride gives rise to both CO and CO_2 . Activated carbon has any of the following namely: protonated (C–OH₂⁺) known as H-type carbons, or neutral (COH), or ionized (CO⁻) referred to as L-type carbons on its surface. Several IR-active functional groups that can be seen at the edges of and within grapheme layers of activated carbon after the oxidative treatment are depicted in Figure 3 [21; 23].

Yusufu luka et al., The Promising Precursors for Development of Activated Carbon: Agricultural Waste ...

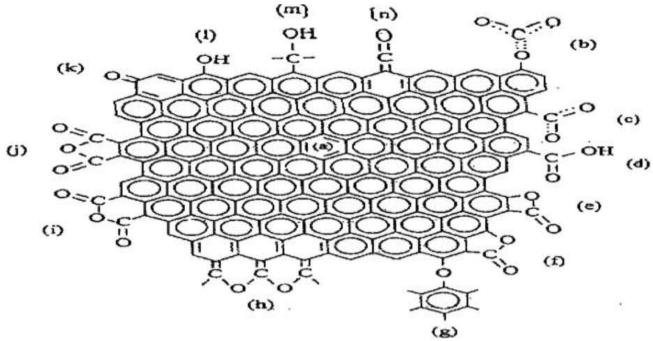


Figure 3: IR-active functional groups on carbon surface: (a) aromatic C=C stretching; (b) and (c) carboxyl-carbonates; (d)carboxylic acid; (e) lactone(4-memberedring); (f) lactone(5-memberedring); (g)ether bridge; (h) cyclic ether;(i) cyclic anhydride (6-membered ring); (j) cyclic anhydride (5-membered-ring);(k) quinine; (l) phenol; (m) alcohol; and(n) ketene [23].

3. AGRICULTURAL WASTE MATERIALS

Activated Carbon obtained from agricultural by product has the advantage of offering an effective low cost replacement for nonrenewable coal-based granular activated carbons provided that they have similar or better adsorption efficiency [10; 14; 20; 24]. Agricultural waste materials are considered as very important feedstock as they are renewable and low-cost materials. Activated carbon is a well-known material with complex pore structure, large specific surface area, good chemical stability, and various oxygen-containing functional groups on the surface. These excellent features have made it widely used in environmental protection, water and wastewater treatment and gas filters. The qualities and characteristics of activated carbon produced from any precursor including agricultural waste materials depend not only on the physical and chemical properties of the initial material but also on the activation methods used [25; 26]. To utilize cheap and abundant agricultural waste materials, it is promising to convert agricultural waste into activated carbon. This conversion will address problems associated with unwanted agricultural wastes been converted into useful, value- added adsorbent and also the use of agriculture by- products to represent potential source of adsorbent which will largely address problems associate with environmental pollution and waste management[13; 27; 28].

A group of researcher in the north eastern part of Nigeria in Maiduguri Bornu State carried out an investigation on a local agricultural waste material known as groundnut shells which was used to produce activated carbon using phosphoric acid as activating agent. The activated carbon developed was later applied for removal of iron and manganese in raw water [13]. The results obtained during the investigation are presented in Table 1 and show that agricultural waste materials such as ground nut shells are promising precursor for the development of activated carbon.

S/No	Parameters	Results	
1	PH	6.8	
2	Moisture content (%)	15	
3	Volatile matter (%)	11	
4	Ash content (%)	6	
5	Carbon content (%)	68	
6	Bulk density(g/L)	420	
7	Electrical conductivity(µS/cm)	824	
8	Surface area (m^2/g)	975	
9	Adsorption capacity of Mn and Fe(mg/g)	55.5 and 130.5	
10	% adsorbed of Mn and Fe	84. and 90	

Table1: Characterization of Groundnut Shell Activated Carbon and Trea	atment Efficiency [13].
---	-------------------------

A group of investigators [29] carried out a research on the use of cassava peel to develop activated carbon for use in effluent treatment. The cassava peel was obtained from the wastes of cassava processing and was carbonized at different temperatures between 200 °C and 400 °C for 15, 30, 45 and 60 min in order to determine the optimal conditions for the pre-treatment of the cassava peels. The chemical activations of the resulting carbons were carried out using different concentrations of H_2SO_4 , HCl and ZnCl₂ from 0.5 to 1.5M. The results showed that the optimum carbonization temperature and time for the preparation of good cassava peel activated carbon (CPAC) with high fixed content were 350 °C and 45 min, respectively. Also, characterizations results revealed that a promising quality activated carbon from cassava peel was able to be prepared using zinc chloride with1.0M concentration and were found to be in good agreements with the literature values. The results are presented in Table 2.

S/N		-	Experimental value		
	Property	Unit	CPAC at 350 °C, 45 min with 1.0 M ZnCl ₂	Literature value	
1.	Moisture content	%	1.20	2-8	
2.	Ash content	%	5.90	≤ 8	
3.	Volatile content	%	13.5	< 20	
4.	Fixed carbon	%	87.40	>75	
5.	Pore volume	cm ³	1.15	1.109	
6	Porosity	mL/g	0.198	0.214	
7.	Bulk density	g/cm ³	0.38	0.4-0.5	
8.	Charcoal yield	%	34.0	39.99- 55.44	

Table 2: Parameters of Cassava Peel Activated Carbon at Optimum Percentage Fixed Carbon [29]

It was reported that results obtained by some researchers [21] on characterizations of agricultural waste materials from different community are presented in Table 3. They records made show that agricultural waste materials meets all the criteria required for development of activated carbon and are indeed the promising precursors for development of activated carbon.

Table 3: Proximate and Ultimate Analysis for some Selected Agricultural Waste Materials [21].

Agricultural waste	Proximate analysis (% w/w)			Ultimate analysis (% w/w)				
	Moisture	Ash	Volatiles	с	н	Ν	S	0
Palm shell	7.96	1.10	72.47	50.01	6.9	1,9	0.0	41
Palm stem	6.06	4.02	72.39	45.56	5.91	0.82	-	47.71
Grape stalk	15.69	10.16	51.08	46.14	5.74	0.37	0.0	36.60
Bamboo	7	3.90	80.6	43.8	6.6	0.4	0.0	-
Coconut shell	8.21	0.1	73.09	48,63	6.51	0.14	0.08	44.64
Olive mill	< 5.0	< 1.0	<u> </u>	45.64	6.31	1.42	2	124
Almond shell	10.00	0.60	80.30	50.50	6.60	0.20	0.01	42.69
Wallnut shell	11.00	1.30	71.80	45.10	6.0	0.3	0.0	48.60
Almond tree pruning	10.60	1.20	72.20	51.30	6.50	0.80	0.04	41.36
Olive stone	10.40	1.40	74.40	44.80	6.0	0.1	0.01	49.09
Bamboo	2.44	6.51	69.63	45.53	4.61	0.22	57	0.770
Durian shell	11.27	4.84		39.30	5.90	1.00	0.06	53.74
Chinese fir sawdust	4.88	0.32	79.92	48.95	6.54	0.11	0.00	39.20
Banana empty fruit bunch	5.21	15.73	78.83	41.75	5.10	1.23	0.18	51.73
Delonix regia fruit pods	0.22	2.80	92.03	34.22	4.50	1.94	0.42	58.91
Corn cob	4.3	0.90	78.7	46.8	6.0	0.9	-	46.3
Pomegranate seed	5.38	1.83	78.71	49.65	7.54	4.03	0.65	38.13
Birch	4.4	0.18		48.4	5.6	0.2	-	45.8
Salix	7.3	0.75	~	48.8	6.2	1.0	~	43.4
Sugarcane bagasse	6.2	0.90	<u>1</u>	47.3	6.2	0.3	14 14	46.2
Wheat straw	3.3	3.23	-	46.5	6.3	0.9	-	46.3
Bagasse	2	6.2	83.3	41.55	5.55	0.03	2	52.86
Rice husk	-	16.7	67.5	36.52	4.82	0.86	Ξ	41.10
Cassava peel	11.4	0.3	59.4	59.31	9.78	2.06	0.11	28.74
Rice stalk	14.17	14.93	66.33	40.79	7.66	1.17	0.49	49.89
Woody birch	6.6	0.2	81.2	48.4	5.6	0.2	-	45.8

In a nut shell, according to [21] any inexpensive material with high carbon and a low inorganic content can be used as a precursor for activated carbon productions as well as lignocellulosic material. They concluded that there are two main sources of activated carbon production; coal and agricultural by products or lignocellulosic materials. In addition, the reporters [21] explained that carbon contents from agricultural materials or by-products are lower as compared to anthracite, coal or peat because the yields of the activated carbon from agricultural material precursors are expected to be lower. Nevertheless, the availability of agricultural materials or wastes and useful of the end products of the waste, particularly activated carbon, and the economic input that can be achieved from these useful products eventually can off-set the costs of treatment and disposal. Based on literature [30], it was concluded in their report that employing agricultural waste to produce activated carbon which are further used in various fields, is not only a promising exploration but also economically viable and sustainable for the environment.

4. STEPS INVOLVED IN DEVELOPMENT OF ACTIVATED CARBON

Many researchers reported that there are two main steps for the development of activated Carbon which include the carbonization of the carbonaceous raw material and the activation of the char [20; 31; 32; 33]. The carbonization step consists of a pyrolysis procedure, in which, volatile compounds are released due to several complex, rival, and consecutive reactions leading to the achievement of fixed carbon in the absence of oxygen (an inert atmosphere) and at temperature below 800 °C [32] that is range of 400 - 500 °C [33]. Concerning activation, it is usually by either physical or chemical process. A researcher [11] reported that the temperature for carbonization range from 600 - 800 °C and for gasification is between 800 - 1000 °C for physical activation, while chemical activation needs a temperature of 500 - 800 °C. The entire process for activation is presented in Figure 4.

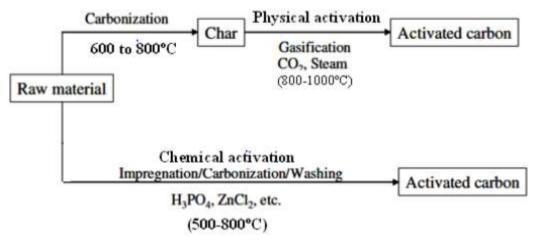


Figure 4: General Schematic Representation of the Process of Activated Carbon Development [11].

For physical activation process sometimes called pyrolysis process, the precursor is placed under a heat treatment at high temperatures from 700 - 1100 °C in the presence of oxidizing agents, such as CO₂, water steam, air, or a mixture of them to increase the porosity and surface area [18; 20; 34]. It was further explained [33] that physical activation is a two-step process which involves carbonization of raw materials followed by activation of the resulting char. Whereas the literature [35] reported that despite two-step carbonization and activation using steam or carbon dioxide as the activation agent is the most commonly used process for physical activation, the single step physical activation is able to produce activated carbon with excellence properties using coconut shell which give result comparable with the two step approaches. Figure 5 represents an experimental set up for physical activation with carbon dioxide gas for development of activated Carbon from sugarcane bagasse while Figure 6 depicts basic flow sheet for physical activation for development of activated carbon, respectively.

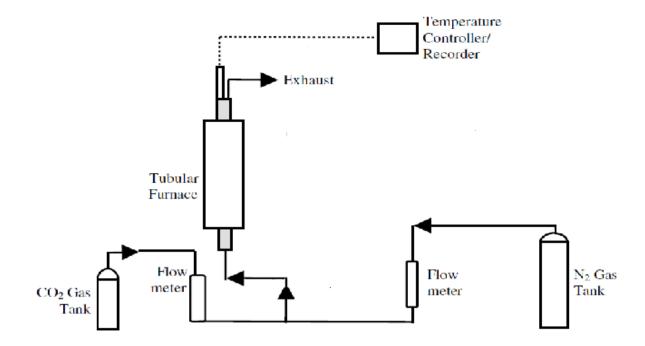


Figure 5: Showing Setup for the Development of Activated Carbon Using Physical Activation [33].

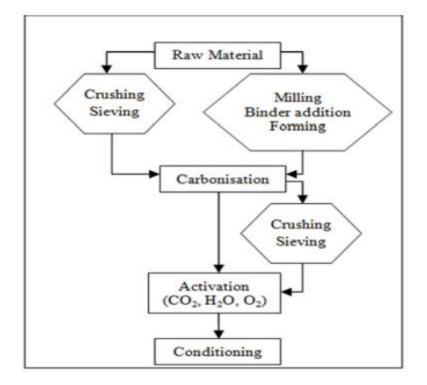


Figure 6: Basic Flow Sheet for Physical Activation for Development of Activated Carbons [34].

In chemical activation both activation and carbonization is occurring simultaneously [20; 33], the precursor is mixed with a certain amount of active agents such as KOH and NaOH, H_2SO_4 , HCl, H_3PO_4 , and ZnCl₂, which lead to the development of porous structures in the material [18; 27; 33; 36]. Chemical activation causes both the physical and chemical modifications of the activated carbon developed [20]. There are different kinds of dehydrating agents used for chemical activation but phosphoric acid is preferred recently due to environmental and economic concerns [37; 38]. Phosphoric acid compared to zinc chloride is the most preferred because of the environmental disadvantages like the problem of corrosion and inefficient chemical recovery associated with zinc chloride. In addition, the activated carbons developed by using zinc chloride as an activating agent though as higher specific area than those obtained from phosphoric acid cannot be used in pharmaceutical and food industries as they may contaminate the product [39]. Phosphoric acid allows the developing of both micropores and mesopores of the resulting activated carbon [18; 21]. Chemical activation has several advantages which include single step activation [33]; the process is carried out at lower temperatures, higher yields, than physical activation process. The activating agents act as dehydrating agents that inhibit the

formation of tar as well as volatile substances during the process, which helps to enhance the yield of porous carbon and to decrease the activation temperature and activation time compared with the physical activation method [18; 33]. However, chemical activation process involves a complex recovery and recycle of the activating agent, which generates liquid discharge that demands effluent treatment [33]. Figure 7 explain an experimental set up used for a series of different activated carbons monolith of both honeycomb and disc type developed by chemical activation of coconut shells with zinc chloride at different concentrations, without the use of a binder and Figure 8 gives a basic flow sheet for chemical activation for development of activated carbon, respectively.

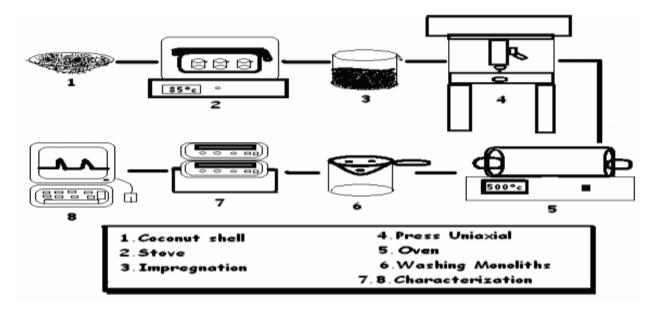


Figure 7: Schematic Representation for the Development of Activated Carbon Using Chemical Activation [22].

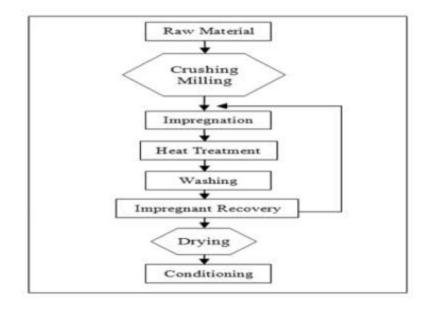
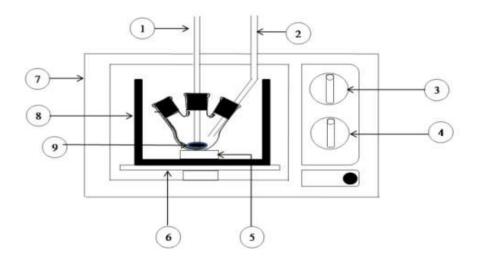


Figure 8: Basic flow Sheet for Chemical Activation for Development of Activated Carbons [34].

Moreover, conventional during the development of activated carbon, heat is transferred by conduction, convection and radiation mechanisms to the raw materials or precursors of interest which resulted to the heating of the surface of the particle before their interior and causes a thermal gradient between the surface and core of the particle. The induced thermal gradient gives room to an inhomogeneous microstructure for high heating rate. Microwave irradiation is a modern process of heating which gives better low cost and homogeneous activated carbon with high energy savings. This is achieved by direct heating of sample interior by microwave heating which induces rapid volumetric heating [40]. Based on research [40] relatively to conventional heating Processes, microwaves activated carbon developed from apple pulp and apple peel using phosphoric acid as activating agent show a high BET surface areas and mesopore volumes after a shorter activation time due to differences in the type of heat transfer

between these two processes. In addition, a group of researcher [41] carried out an investigation using waste palm kernel shells and was able to obtain microwave-induced high surface area; chemical activated carbon successfully developed using phosphoric acid. The microwave developed activated carbons were characterized using Fourier Transform Infrared Spectroscopy, Nitrogen Gas Adsorption analysis and Thermal Analysis respectively. The result obtained from the chemical characterization ascribe that the type and concentration activation process influenced the chemical and physical properties of activated carbon. It was observed that the microwave activated carbon with 60 % concentration of phosphoric acid used gives the best developed activated carbon with 630 m^2/g surface area compared to the others. They concluded that the microwave induced technique is a potential alternative and simpler method in developing activated carbon from agriculture waste. Figure 9 gives a simple diagram of microwave for development of activated carbon from waste palm kernel shells.



Legend:

Gas inlet (2) Gas outlet (3) Variable power control knop (4) Timmer knop (5) Dummy block (6) Turnable (7) Microwave (8) Insulator (9) Sample



5. CHARACTERIZATION AND PROPERTIES OF ACTIVATED CARBON

The activated carbon developed need to be characterized and the properties is obtained to know its suitability for various application. Activated Carbon texture characteristics and surface properties depend on the precursor and process used for its development [28]. In addition, an investigator [23] reported that basically, the characteristic of activated carbon depends on the physical (bulk density, moisture content, volatile matter content, ash content, and surface area and porosity) and chemical properties of the precursor as well as activation process used. The researcher further explained that Physical properties of activated carbon, such as ash content and moisture content can affect their use and render them either suitable or unsuitable for specific applications. Whereas, the specific surface area of activated carbon also can be characterize by various strategies such as adsorption of gases(N₂, Ar, Kr, CO₂) or vapors (benzene, water), scanning electron microscopy(SEM) and transmission electron microscopy (TEM) [23].

Not forgotten, characterization of activated carbon can also be investigated by: (a) proximate analysis (moisture content, volatile matter content, ash content, and fixed carbon);(b) ultimate (elemental) analysis which determine the composition of activated carbon (Carbon, Hydrogen, Nitrogen and Sulphur);(c) Fourier Transform Infrared (FTIR) analysis for analyzing surface chemistry and used to detect the functional groups present in any developed activated carbon ; (d) X-Ray diffraction where the sharp peak is produced due to better layer alignment which is the characteristic of a crystalline structure. Absence of sharp peaks in activated carbon suggests it is predominantly amorphous structure which is advantageous property for well-defined adsorbents; (e) Thermo gravimetric analysis which means the degradation of weight with respect to temperature and time. This process helps to determine the range of working temperature to work on; (f) Methylene blue adsorption due to its strong adsorption onto solids, Methylene blue dye serves as a model compound for adsorption of organic contaminant; and(h) Iodine removal [24; 28; 42].

6. APPLICATIONS OF ACTIVATED CARBON AND CONTACTORS USED

Activated carbon has various applications which vary from liquid to gaseous - phase such as in domestic, commercial and industrial settings [21; 36]. Physical properties of activated carbon play a vital role in determining its best application. For instance, if the activated carbon is intended for an application in which frequent back-washing is needed, the hardness or abrasion resistance properties are very important for the activated carbon. If the activated carbon is used for gaseous and vapours, its porosity with radii less than 16–20 Å is required. If the activated carbon is intended for colour removal in liquid phase system, its porosity with radii in the range of 20–500 Å is needed [21]. Nevertheless, the chemical nature of activated carbon significantly influences the following: it's adsorptive, electrochemical and catalytic properties that is to say activated carbon with acidic surface chemical properties are favourable for basic gas adsorption such as ammonia while that with basic surface chemical properties are suitable for acidic gas adsorption such as sulphur dioxide [32]. In food industries, activated carbon can be utilized for decolourization, deodorization and taste removal purposes; in medicine field, it is used for removal of harm full chemical and drug, for instance, the removal of toxic from the blood of patients and recovery of poison by oral ingestion into the stomach; in gas cleaning applications, activated carbon is used for air filters and air conditioning purpose and in mineral industry, for gold recovery from leached liquors [21; 36].

Generally Speaking, major applications of activated carbon can be considered or looked at from two perspectives namely gaseous phase and liquid phase. Activated carbon application in gas phase includes separation, gas storage and catalysis [9]. Twenty percent of active carbon developed is utilized in gas-phase application of which most is granulated. Separation processes is the main gas-phase applications of activated carbon which has the greatest influence upon gas adsorption. Adsorption in gas-phase is a function of the molecular weight and size of the gas molecule to be adsorbed. Organic molecules with large molecular weight are not readily separated from air by activated carbon. The gaseous-phase applications include the following: Process stream application, Solvent recovery and Protection against atmospheric contaminations. Whereas, the application of activated carbon in differs from gas-phase carbons primarily in pore size distribution. In liquid-phase, adsorption takes place in liquid – phase mesopores which allows liquid to diffuse more rapidly into the mesopores and micropores. The larger pores in mesopores promote greater adsorption of large molecules, either impurities or products of concern. Liquid - phase activated carbon; granular, powdered, or shaped form carbon can be used. The degree of purification required in the adsorption application is an important factor in choosing either powder or non-powder activated carbon. Granular or shaped carbons are used in continuous systems (Fixed bed or Fluidised bed), where the liquid to be treated is passed through a contactor. The influents to be treated are adsorbed by the carbon bed in the adsorption zone [43]. Examples includes: industrial and municipal wastewater treatment [14], drinking water treatment, chemical processing and decolourization of sweetener [36].

There are basically two or more contactors used in application of activated carbon namely batch or semi- batch and continuous contactors. Majority of the investigation on the use of activated carbon was carried out using batch mode due to the ease of operation [44; 45; 46]. Some researchers [46] investigated the suitability of activated *Borassus aethiopum* seed shells (BASS) and *Cocos nucifera* shells (CONS) collected within Zaria, Nigeria and its environs which were crushed into particle size of about 300-450 μ m and used for the removal of Pb (II) and Cd (II) in aqueous solution through batch adsorption studies. The Langmuir and Freundlich isotherm models were used to represent experimental data. Both models were found to fit well based on the high values of the coefficient of regression R². The monolayer adsorption capacity, Q_o for Pb (II) was found to be 12.19 mg/g and 24.39 mg/g and 10.20 mg/g and 25.797 mg/g for Cd (II) for activated BASS and CONS respectively. The Pseudo-second order kinetic model provided best correlation of experimental data for the adsorption of both metal ions (using activated BASS/CONS), whereas the Pseudo-first order model did not fit experimental data well. Also, the Pseudo-second order model was found to be more statistically significant than the Pseudo-first order kinetic model.

Based on the researched [47] carried out on removal of Pb (II) from aqueous systems onto activated carbon and treated activated carbon via batch and column mode studies under various conditions. It probes mainly two adsorbents that is activated carbon: Coconut shell based granulated activated carbon (AC) and modified activated carbon enrich with sulphur (AC–S). Both the adsorbents are subjected to batch mode adsorption studies and then after a comparison based on isotherm analysis; more efficient adsorbent using continuous-flow column operation by varying different operating parameters like hydraulic loading rate ($3.0-10.5m^3/(hm^2)$), bed height (0.3-0.5m) and feed concentrations (2.0-6.0mg/l). At the end, an attempt has also been made to model the data generated from column studies using the empirical relationship based on Bohart–Adams model. The lead removal increased for sample of treated carbon. The contactor (reactor) for the continuous mode is presented in Figure 10.

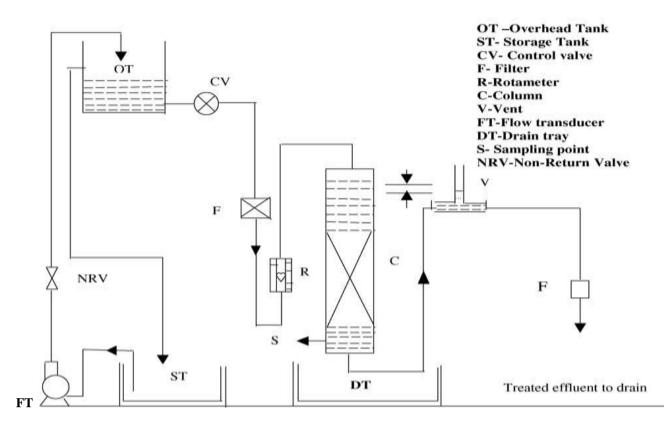


Figure 10: Experimental Setup for Dynamic Column Studies [47].

Moreover, some investigators [48] investigated the performance of fluidised bed reactor (FBR) to remove Ni (II) from the aqueous solution using Granular activated carbon (GAC) as an adsorbent and maximum removal of 75.23% was observed at pH 6. Adsorption of Ni (II) increases with time and with increase in adsorbent dose. But with the increase in initial ion concentration of Ni (II), the rate of removal decreases. Figure 11 shows the schematic representation of the process involved in removal of Ni (II) from aqueous systems.

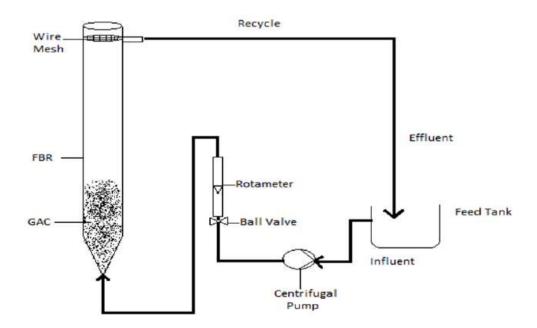


Figure 11: Schematic Representation of Laboratory Scale Fluidised Bed Reactor [48]

7. CONCLUSION

The following conclusion can be drawn from the reviewed made on agricultural waste materials as promising precursors for development of activated carbon:

- i. Activated carbon is known as a carbonaceous material showing a well-developed surface area and porous texture. The surface is a significant characteristic of the activated carbon which has a typical range of $500 1000 m^2/g$ and the porous structure can be classified into three major groups namely: micropores with a pore width of less than $2.0 \times 10^{-9} m$, mesopores with widths from $2.0 to 50.0 \times 10^{-9} m$ and macropores with a pore width larger than $50.0 \times 10^{-9} m$.
- ii. Activated carbon is a black solid substance, amorphous, microcrystalline, a non-graphite form of carbon and tasteless as well as it cannot be converted into crystalline graphite even at temperature above 3000 °C. Activated carbon is associated with heteroatoms like oxygen, sulfur, hydrogen, nitrogen, halogen and other elements in the forms of functional groups and/or atoms which bonded chemically to the structure.
- iii. Agricultural waste materials are considered as very important and promising precursors due to their availability, renewability, economically viable and sustainable for the environment. Apart from utilizing cheap and abundant agricultural waste, it is promising indeed to convert agricultural waste into activated carbon. This conversion will address problems associated with unwanted agricultural wastes been converted into useful, value- added adsorbent and also the use of agriculture by- products to represent potential source of adsorbent which will largely address problems associate with environmental pollution and waste management.
- iv. Carbonization of the carbonaceous raw material and the activation of the char are the two major steps involved in development of activated carbon. The carbonization step leads to the achievement of fixed carbon in an inert atmosphere and at temperature below 800 °C. Concerning activation, it is usually by either physical or chemical process.
- v. The characteristic and properties of activated carbon depends on the physical and chemical properties of the precursor as well as activation process used.
- vi. Activated carbon has various applications which comprise removal of organic and inorganic compound from liquid and gaseous streams. Some of the fields where activated carbons are used include: waste water treatment, food industries, gas cleaning applications and mineral industry. The contactor used during applications of activated carbon is either batch or continuous.

8. RECOMMENDATION

Based on this review the following recommendation can be made:

- i. There is the need to carry out more detailed investigations on the available agricultural waste materials in every community to determine the suitability for development of activated carbon and add value to the waste generated from agricultural practice which end up polluting the environment.
- ii. A comprehensible research need to be carried out on each agricultural waste material to ascertain the optimal conditions for development and characterization of the agricultural base precursor for better application of each activated carbon derived from the agricultural waste.
- iii. The right analysis should be carried out for each reactor or contactor used on the course of applying any activated carbon. For example, continuous contactor required breakthrough curves analysis whereas batch or static mode Performance need adsorption isotherm such as Langmuir and Freundlich model and adsorption kinetics like Pseudo-first-order, Pseudosecond-order and Intra particle diffusion model.

REFERENCES

- [1]. Foo, P.Y L. and Lee, L. Y. (2010). Preparation of Activated Carbon from Parkia Speciosa Pod by Chemical Activation. Proceedings of world Congress on Engineering and Computer Science Vol. II, pp. 20-22, San Francisco, USA.
- [2]. Alothman, Z. A., Habila, M.A. and Ali, R. (2011). Preparation of Activated Carbon Using the Copyrolysis of Agricultural and Municipal Solid Wastes at a Low Carbonization Temperature. International Conference on Biology, Environment and Chemistry IPCBEE Vol.24, IACSIT Press, Singapoore, Pp. 67-72.
- [3]. Wang, J., Wu, F., Wang, M., Qiu, N., Liang, Y., Fang, S. and Jiang, X. (2010). Preparation of Activated Carbon from a Renewable Agricultural Residue of Pruning Mulberry Shoot. African Journal of Biotechnology Vol. 9 (19), Pp. 2762-2767.

- [4]. Chowdhury, Z. Z., Hamid, S. B. A., Das, R., Hassan, M. R., Zain, S. M., Khalid, K. and Uddin, M. N. (2013). Preparation of Carbonaceous Adsorbents from Lignocellulosic Biomass and Their Use in Removal of Contaminants from Aqueous Solution: Review Article, Biosciences, Vol. 8(4), Pp. 6523-6555.
- [5]. Kaale, L. D. and Katima, J. H. Y. (2013). Performance of Activated Carbons in the Catalytic Wet Peroxide Oxidation (CWPO) of Maleic Acid. Journal of Engineering and Technology Research, Vol. 5(6), Pp.189-199, DOI: 10.5897/JETR09.061.
- [6]. Gumus, R. H. and Okpeku, I. (2015). Production of Activated Carbon and Characterization from Snail Shell Waste (*Helix pomatia*). Advances in Chemical Engineering and Science, Vol. 5, Pp. 51-61. Available online at http://dx.doi.org/10.4236/aces.2015.51006
- [7]. Dias, J. M, Alvim-Ferraz, M. C. M, Almeida, M. F., Rivera-Utrilla, J, Sa'nchez-Polo, M. (2007). Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. Journal of Environmental Management, Vol. 85, Pp. 833–846.
- [8]. Rengga, W.D.P., Sudibandriyo, M and Nasikin, M. (2012). Development of Formaldehyde Adsorption using Modified Activated Carbon A Review. International Journal of Renewable Energy Development, Vol. 1 (3), Pp. 75-80.
- [9]. Rashidi, N. A., Yusup, S. and Borhan, A. (2014). Development of Novel Low-Cost Activated Carbon for Carbon Dioxide Capture. International Journal of Chemical Engineering and Applications, Vol. 5(2), Pp. 90-94.
- [10]. Nhapi, I., Banadda, N., Murenzi, R., Sekomo, C. B. and Wali, U. G. (2011). Removal of Heavy Metals from Industrial Wastewater Using Rice Husks. The Open Environmental Engineering Journal, Vol. 4, pp. 170-180.
- [11]. Mohamed, E. F. (2011). Removal of Organic Compound from Water by Adsorption and Photocatalytic Oxidation. Thése, En Vue de l' Obtention du Doctorat de l' Université de Toulouse, Génie des Procédés de l'Environnement. PP. 1-253.
- [12]. Ketcha, J. M., Dina, D. J. D., Ngomo, H. M. and Ndi, N. J. (2012). Preparation and Characterization of Activated Carbons Obtained from Maize Cobs by Zinc Chloride Activation. American Chemical Science Journal, Vol. 2(4), Pp. 136-160, 2012.
- [13]. Aji, M. M., Gutti, B. and Highina, B. K. (2015). Production and Characterization of Activated Carbon from Groundnut Shell Sourced in Maiduguri. Columban Journal of Life Science, Vol. 17(1), pp. 18-24.
- [14]. Al-Doury, M. M. I. and Ali, S. S. (2015). Removal of Phenol and Parachlorophenol from Synthetic Waste water Using Prepared Activated Carbon from Agricultural Wastes. International Journal of sustainable and Green Energy, Vol. 4(3), pp.92-101.
- [15]. Bhatnagar, A. and Minocha, A. K. (2006). Conventional and Non-conventional Adsorbents for Removal of Pollutants from Water: A Review. Indian Journal of Chemical Technology, Vol. 13, Pp. 203-217.
- [16]. Menéndez-Díaz, J. A. and Martín-Gullón, I. (2006). Types of carbon Adsorbents and their Production: Published in Activated Carbon Surfaces in Environmental Remediation (Interface Science and Technology, Series, 7) Bandosz, T., Ed. Elsevier, Pp. 1-48.
- [17]. Aznar, J. S. (2011). Characterization of Activated Carbon Produced from Coffee Residues by Chemical and Physical Activation. Master Thesis, Chemical Engineering, KTH Chemical Science and Engineering, Stockholm, Sweden, Pp. 1-66.
- [18]. Kumar, A. and Jena, H. M. (2016). Preparation and characterization of high surface area activated carbon from Fox nut (Euryale ferox) shell by chemical activation with H₃PO₄. Results in Physics, Vol. 6, Elsevier, Pp. 651–658.
- [19]. Pastor-Villegas, J., Pastor-Valle, J.F., Rodri'guez, J.M. M., and Garci'a, M. G. (2006). Study of Commercial Wood Charcoals for the Preparation of Carbon adsorbents. Journal of Analytical and Applied Pyrolysis, Vol. 76, Pp. 103–108.
- [20]. Amirza, M. A. R., Adib, M. M. R. and Hamdan, R. (2017). Application of Agricultural Wastes Activated Carbon for Dye Removal – An Overview. MATEC Web of Conferences Vol. 103 (06013), Pp. 1-12, DOI: 10.1051/matecconf/20171030.
- [21]. Yahya, M. A., Al-Qodah, Z., and Ngah, C.W.Z. (2015). Agricultural Bio-waste Materials as Potential Sustainable Precursors used for Activated Carbon Production: A review. Renewable and Sustainable Energy Reviews, Vol. 46, Pp. 218–235.
- [22]. Vargas-Delgadillo, D. P., Giraldo, L., and Moreno-Piraján, J. C. (2010). Preparation and Characterization of Activated Carbon Monoliths with Potential Application as Phenol Adsorbents. E-Journal of Chemistry, Vol. 7(2), Pp. 531-539. Available online at <u>http://www.e-journals.net</u>.

- [23]. Jabit, N. B. (2007). The Production and Characterization of Activated Carbon Using Local Agricultural Waste through Chemical Activation Process. Master of Science Thesis, School of Material and Mineral Engineering, Universiti Sains Malaysia, Pp. 1-24.
- [24]. Sugumaran, P., Susan, V. P., Ravichandran, P. and Seshadri, S. (2012). Production and Characterization of Activated Carbon from Banana Empty Fruit Bunch and *Delonix regia* Fruit Pod. Journal of sustainable Energy and Environmental, Vol. 3, pp. 125-132.
- [25]. Girish, C. R. and Murty, V. R. (2012). Adsorption of Phenol from Wastewater Using Locally Available Adsorbents. Review Paper. Journal of Environmental Research and Development Vol. 6 (3A), Pp. 763-772.
- [26]. Patil, B. S. and Kulkarni, K. S. (2012). Development of High Surface Area Activated Carbon from Waste Material: Review Article. International Journal of Advanced Engineering Research and Studies, Vol. I (II), Pp. 109-113.
- [27]. Kwaghger, A. and Ibrahim J.S. (2013). Optimization of Conditions for the Preparation of Activated Carbon from Mango Nuts using HCl. American Journal of Engineering Research, Vol. 2(7), Pp. 74-85.
- [28]. Das, D, Samal, D. P. and Meikap B. C. (2015). Preparation of Activated Carbon from Green Coconut Shell and its Characterization. Journal of Chemical Engineering and Process Technology, Vol. 6(5): 248, Pp.1-7, Doi:10.4172/2157-7048.100024.
- [29]. [Gin, W. A., Jimoh, A., Abdulkareem, A. S. and Giwa, A. (2014). Utilization of Cassava Peel Waste as a Raw Material for Activated Carbon Production: Approach to Environmental Protection in Nigeria. International Journal of Engineering Research and Technology, Vol. 3 (1), Pp. 35-42.
- [30]. Malhotra, P., Payal, R. and Jain, A. (2016). Whether to Worry with Waste: A Review on Activated Carbon Precursors from Various Waste Materials. International Journal of Advanced Research, Vol. 4(1), Pp. 14- 20.
- [31]. Mart'inez, M.L., Torres, M.M., Guzm'an, C.A., and Maestri, D.M. (2006). Preparation and Characteristics of Activated Carbon from Olive Stones and Walnut shells. Industrial Crops and Products, Vol. 23, Pp. 23–28.
- [32]. Ioannidou, O. and Zabaniotou, A. (2007). Agricultural Residues as Precursors for Activated Carbon Production—A review. Renewable and Sustainable Energy Reviews, Vol. 11, Pp. 1966-2005.
- [33]. Sutrisno, B., Rizka, N. A., Hidayat, A. S. and Hidayat, A. (2016). Preparation and Characterization of Activated Carbon from Sugarcane Bagasse by Physical Activation with CO₂ Gas. IOP Conf. Series: Materials Science and Engineering Vol. 105 (012027), Pp. 1-8, doi:10.1088/1757-899X/105/1/012027.
- [34]. Lee, T., Ooi, C.-H., Othman, R. and Yeoh, F.-Y. (2014). Activated Carbon Fiber The Hybrid of Carbon Fiber and Activated Carbon. Reviewed Advanced Materials Science, Vol. 36, Pp. 118-136.
- [35]. Rashidi, N. A., Yusup, S., Ahmad, M. M., Mohamed, N. M. and Hameed B. H. (2012). Activated Carbon from the Renewable Agricultural Residues Using Single Step Physical Activation: A Preliminary Analysis. APCBEE Procedia, Vol. 3, Pp. 84-92.
- [36]. Alkali, A. S. (2016). Optimization of Activated Carbon Preparation from Corncob for Waste water Treatment. Master Dissertation, Department of Chemical Engineering, Faculty of Engineering Ahmadu Bello University, Zaria, Nigeria, Pp. 1-87.
- [37]. Teshome, A. (2015). Preparation, Characterization and Application of Coffee Husk Based Activated Carbon for Adsorption of Cr (VI) From Aqueous Solution. Master Thesis, Environmental Engineering, School Of Chemical and Bio Engineering, Addis Ababa University, Addis Ababa Institute of Technology, Ethiopia, Pp. 1-25.
- [38]. Yashim, M. M., Razali, N., Saadon, N. and Rahman, N. A. (2016). Effect of Activation Temperature on Properties of Activated Carbon Prepared from Oil Palm Kernel Shell (Opks). Journal of Engineering and Applied Sciences, Vol. 11(10), Asian Research Publishing Network (ARPN), Pp. 6389-6392.
- [39]. Al-Qodah, Z. and Shawabkah, R. (2009). Production and Characterization of Granular Activated from Activated Sludge. Brazilian Journal of Chemical Engineering, Vol. 26(1), Pp.127-136.
- [40]. Hesas, R. N., Arami-Niya, A., Wan Daud, W. M. A. and Sahu J. N. (2013). Preparation and Characterization of Activated Carbon from Apple Waste Microwave-Assisted Phosphoric Acid Activation: Application in Methylene Blue Adsorption. Bioresources.com Vol. 8(2), Pp. 2950-2966.
- [41]. Yacob, A. R., Wahab, N. Suhaimi, N. H., and Mustajab, M. K. A. A. (2013). Microwave Induced Carbon from Waste Palm Kernel Shell Activated by Phosphoric Acid. International Journal of Engineering and Technology, Vol. 5(2), Pp. 214-217.

- [42]. Dinesh, S. (2011). Development and Characterization of Pellet Activated Carbon from New Precursor. Bachelor of Technology Thesis, Chemical Engineering, National Institute of Technology, Rourkela, Orissa, India, Pp. 1-54.
- [43]. Tchobanoglous, G., Burton, F. L. and Stensel, H. D. (2003). Wastewater Engineering: Treatment and Reuse, Pp. 1138-1162, Tata McGraw-Hill Publishing Company Limited, New Delhi india.
- [44]. Kadirvelu, K., Kavipriya, M., Karthika, Radhika, M., N. Vennilamani, N and Pattabhi, S. (2003). Utilization of Various Agricultural Wastes for Activated Carbon Preparation and Application for the Removal of Dyes and Metal Ions from Aqueous Solutions. Bioresource Technology, Vol. 87, Pp. 129–132.
- [45]. Badmus, M. A. O., Audu, T. O. K. and Anyata, B. U. (2007). Removal of Lead Ion from Industrial Wastewaters by Activated Carbon Prepared from Periwinkle Shells (*Typanotonus fuscatus*). Turkish Journal of Engineering and Environmental Science, Vol. 31, Pp. 251 – 263.
- [46]. Adie, D. B., Okuofu, C. A., Osakwe, C. (2012). Isothermal and Batch Adsorption Studies of the Use of *Borassus Aethiopium* and *Cocos Nucifera* for Wastewater Treatment. American International Journal of Contemporary Research, Vol. 2 (7), Pp. 119-130.
- [47]. Goel, J., Kadirvelu, K., Rajagopal, C. and Garg, V. K. (2005). Removal of Lead (II) By Adsorption Using Treated Granular Activated Carbon: Batch And Column Studies. Journal of Hazardous Materials, Vol. B125, Pp. 211–220.
- [48]. Lakherwal, D., Rattan, V. K. and Singh, H.P. (2016). Studies on Adsorption of Nickel by Activated Carbon in a Liquid Fluidised Bed Reactor. Canadian Chemical Transactions, Vol. 4(1), Pp. 121-132.