PREPARATION, CHARACTERIZATION AND EVALUATION OF OPTIMAL ACTIVATED CARBONS DERIVED FROM *PROSOPIS AFRICANA* SEED HULLS FOR THE REMOVAL OF CHLOROPHENOLS FROM AQUEOUS SOLUTION

by

ZAHARADDEEN NASIRU GARBA

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LIST OF ABBREVIATIONS

Symbol	**Description**
AC	Activated carbon
ACs	Activated carbons
AGS	Anaerobic granular sludge
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CAC	Commercial activated carbon
CBAC	Corncob-based activated carbon
CCD	Central composite design
CFAC	Cattail fibre-based activated carbon
CH_3COONa-AC	Optimal activated carbon with sodium acetate
CSAC	Coconut shell activated carbon
CHAC	Coconut husk-based activated carbon
CP	Chlorophenol
CPs	Chlorophenols
CS-SA-CD	Chemically modified chitosan
DOE	Design of experiment
DS-AC	Date stone activated carbon
FR	Freundlich Isotherm
FTIR	Fourier transmission infrared
GAC	Granular activated carbon
HPO	High pressure oxygen

IR	Impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
K_2CO_3-AC	Optimal activated carbon with potassium carbonate
$K_2C_2O_4$-AC	Optimal activated carbon with potassium oxalate
L1-L5	Langmuir adsorption isotherm (1-5)
LAC	Loosestrife activated carbon
MPP	Modified plantain peel
Np	Number of points
OPEFB-AC	Oil palm empty fruit bunch activated carbon
OPSAC	Oil palm shell activated carbon
PASH	*Prosopis africana* seed hull
PASH-AC	*Prosopis africana* seed hull derived activated carbon
pHzpc	Potency of hydrogen point of zero charge
PPC	Palm pith carbon
rpm	Revolution per minutes
RSBC	Rice straw based carbon
RSD-AC	Rattan sawdust based activated carbon
RSM	Response surface methodology
RDW-AC	Refused derived waste activated carbon
SEM	Scanning electron spectroscopy
TGA	Thermogravimetric analysis
TM	Temkin Isotherm
USA	United States of America

Y	Response
Y_{PASH}	Percentage yield the activated carbon
Y_{4CP}	Percentage 4-Chlorophenol adsorption
Y_{DCP}	Percentage 2,4-Dichlorophenol adsorption
Y_{TCP}	Percentage 2,4,6-Trichlorophenol adsorption
Y_{4C2MP}	Percentage 4-chloro-2-methoxyphenol adsorption
2,4-DCP	2,4-Dichlorophenol
2,4,6-TCP	2,4,6-Trichlorophenol
2CP	2-Chlorophenol
2FI	Two factor interaction
4C2MP	4-chloro-2-methoxyphenol
4CG	4-Chloroguaiacol
4CP	4-Chlorophenol

LIST OF SYMBOLS

Symbol	Description	Unit
A	Temkin constant related to equilibrium binding energy	L g^{-1}
A_i	Absorbance	-
B	Temkin constant related equilibrium heat of sorption	J mol^{-1}
b_o	Response model constant coefficients of design expert	-
b_{ii}	The quadratic coefficients	-
b_{ij}	The interaction coefficients	-
b_T	Temkin constant related to heat of sorption	J mol^{-1}
B_t	Boyd model constant	-
c	Solute or analyte concentration	mg L^{-1}
C_{ad}	Concentration adsorbed	mg L^{-1}
C_d	Effluent sorbate concentration at minimum level	mg L^{-1}
C_e	Chlorophenols concentration at equilibrium	mg L^{-1}
C_i	Intraparticle diffusion model constant	-
C_o	Chlorophenols concentration at equilibrium	mg L^{-1}
ΔG	Gibbs free energy	kJ mol^{-1}
ΔH	Enthalpy change	kJ mol^{-1}
K_F	Freundlich isotherm constant	$(mg^{1-n}\ g^{-1}L^{n})$
K_L	Energy of adsorption for Langmuir isotherm	L mg^{-1}
k_{ip}	Diffusion rate constant	mg g^{-1} $h^{0.5}$
k_1	Pseudo-first-order kinetic constant	h^{-1}
k_2	Pseudo-second-order kinetic constant	g mg^{-1} h^{-1}
m	Mass of adsorbent	g
n	Adsorption intensity related to Freundlich isotherm	-
n_c	Number of center point	-
N	Number of data points	-

p	Path length of cell	cm
Q_a^0	Monolayer adsorption capacity related to Langmuir isotherm	mg g^{-1}
q_e	Adsorption uptake at equilibrium	mg g^{-1}
q_t	Adsorption uptake at time t	mg g^{-1}
q_{cal}	Calculated adsorption capacity	mg g^{-1}
q_{exp}	Experimental adsorption capacity	mg g^{-1}
R	Gas constant	J mol^{-1} K
R^2	Correlation coefficients	-
R_L	Dimensionless separation factor	-
ΔS	Entropy change	J mol^{-1} K
t	Time	h
T	Absolute temperature	K
V	Volume of solution	L
W	Mass of adsorbent	g
x_i, x_j	The coded values of the variables considered	-
Y	The predicted response	-

Greek lette

α	Distance of axial point from centre	cm
χ^2	Chi-square	-
λ	Wavelength	cm
a cm^{-1}	Molar absorptivity	L mg^{-1}

PENYEDIAAN, PENCIRIAN DAN PENILAIAN KARBON TERAKTIF YANG OPTIMUM DARIPADA SEKAM BENIH *PROSOPIS AFRICANA* BAGI PENYINGKIRAN KLOROFENOL DARIPADA LARUTAN BERAIR

ABSTRAK

Potensi sisa pertanian di Nigeria sebagai satu pelopor baharu telah dimanfaatkan untuk menyediakan karbon teraktif untuk penjerapan klorofenol daripada sisa air kumbahan sintetik. Karbon teraktif yang optimum disediakan melalui pengaktifan fizikokimia daripada sekam benih *Prosopis africana* sebagai prekursor baharu menggunakan kalium oksalat, natrium asetat dan kalium karbonat sebagai ejen pengaktifan kimia. Pembolehubah yang dioptimumkan ialah suhu pengaktifan, masa pengaktifan dan nisbah impregnasi kimia; dan responsnya adalah hasil dan peratus penjerapan klorofenol. Keadaan yang optimum adalah 780 ^{o}C, 3.19 IR dan 63 min, 795 ^{o}C, 2.45 IR dan 62 min serta 800 ^{o}C, 2.70 IR dan 58 min masing-masing bagi $K_2C_2O_4$-AC, CH_3COONa-AC and K_2CO_3-AC yang melambangkan suhu pengaktifan, nisbah impregnasi dan masa pengaktifan. Bahan penjerap telah dicirikan melalui analisis keluasan permukaan BET, mikroskop pengimbasan elektron, inframerah transformasi Fourier, analisis elemen dan analisis proksimat untuk menentukan ciri-ciri fizikal dan kimia mereka. Keluasan permukaan BET yang diperoleh adalah 1095.56, 1085.92 dan 1071.89 $m^2 g^{-1}$ masing-masing bagi $K_2C_2O_4$-AC, CH_3COONa-AC dan K_2CO_3-AC. Julat 30-350 mg L^{-1}, 30-50 ^{o}C dan pH 2-12 telah digunakan untuk mengkaji kesan kepekatan awal, suhu proses dan pH terhadap eksperimen penjerapan kelompok. Peningkatan dalam kepekatan awal klorofenol dan masa sentuhan meningkatkan kadar penjerapan bahan penjerap.

Kecekapan penyingkiran yang tertinggi bagi klorofenol ke atas bahan penjerap adalah pada pH larutan awal yang rendah ($pH \leq 2$) kerana kemudahan pengionan dan variasi permukaan kimia yang dialami pada pH tersebut di atas pemukaan AC. Isoterma keseimbangan kelompok dan maklumat kinetik telah dimodelkan, mekanisme proses, termodinamik dan kajian penjanan semula telah dinilai. Maklumat penjerapan keseimbangan telah dimodel dengan menggunakan lima jenis bentuk persamaan Langmuir linear serta isoterma penjerapan Freundlich dan Temkin. Dalam membandingkan kesepadanan setiap model isoterma, khi kuasa dua (χ^2) telah digabungkan dengan pekali korelasi (R^2) untuk mewajarkan asas pemilihan model penjerapan yang terbaik. Isoterma Langmuir-2>Freundlich>Temkin adalah urutan yang terbaik yang menggambarkan maklumat penjerapan keseimbangan. Model kinetic tertib-pseudo kedua adalah yang terbaik menggambarkan keseluruhan proses penjerapan CP ke atas semua AC. Model peresapan intrapartikel juga telah diaplikasikan untuk mengenal pasti mekanisme penjerapan tetapi daripada plot Boyd, telah didapati bahawa penjerapan klorofenol ke atas semua AC kebanyakannya ditentukan oleh peresapan zarah. Kajian penjerapan termodinamik mendedahkan bahawa proses penjerapan adalah endotermik, spontan dan fizikal. Hasil penjanaan semula menunjukkan bahawa bahan penjerap telah digunakan dengan jayanya untuk lima kitaran penjerapan. Karbon teraktif komersial juga telah dikaji di bawah keadaan yang sama untuk membandingkan kecekapan bahan penjerap yang telah disediakan.

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ABSTRACT

Potentials of an agricultural waste in Nigeria as a new precursor were harnessed for preparation of activated carbon for the adsorption of chlorophenols from synthetic wastewaters. Optimal activated carbons were prepared by physicochemical activation from the seed hulls of *Prosopis africana* as a new precursor using potassium oxalate, sodium acetate and potassium carbonate as the chemical activating agents. The variables optimized were activation temperature, activation time and chemical impregnation ratio (IR); and the responses were yield and chlorophenols percentage adsorption. The optimal conditions were 780 ^{o}C, 3.19 IR and 63 min, 795 ^{o}C, 2.45 IR and 62 min as well as 800 ^{o}C, 2.70 IR and 58 mins for $K_2C_2O_4$-AC, CH_3COONa-AC and K_2CO_3-AC respectively, denoting activation temperature, impregnation ratio and activation time, respectively. The adsorbents were characterized via BET surface area analysis, scanning electron microscopy, Fourier transform infrared, elemental analysis and proximate analysis to determine their physical and chemical characteristics. The BET surface area of 1095.56, 1085.92 and 1071.89 $m^2 g^{-1}$ for $K_2C_2O_4$-AC, CH_3COONa-AC and K_2CO_3-AC respectively were obtained. A range of 30-350 mg L^{-1}, 30-50 ^{o}C and pH 2-12 were used to study the effect of initial concentration, process temperature and pH on the batch adsorption experiments. An increase in the initial concentration of the chlorophenols and contact time increased the adsorption uptake of the adsorbents. Highest removal efficiency of the chlorophenols on to the adsorbents was at lower initial solution pH ($pH \leq 2$) attributed to ease of ionization and surface chemistry variation experienced at that pH on surfaces of the ACs. Batch equilibrium isotherms and kinetics data were modeled, the mechanism of the process, thermodynamic and regeneration studies were evaluated. The equilibrium adsorption data were modelled using five various forms of the linearized Langmuir equations as well as Freundlich and Temkin adsorption isotherms. In comparing the suitability of each isotherm model, chi square (χ^2) was incorporated with the correlation coefficient (R^2) to justify the basis for selecting the best adsorption model. Langmuir-2>Freundlich>Temkin isotherms was the best order that described the equilibrium adsorption data. Pseudo-second-order kinetic model best described the entire CPs adsorption processes on all the ACs. Intraparticle diffusion model was also applied to identify the adsorption mechanism but from Boyd plot, it was found that the chlorophenols adsorption on all the ACs was mainly governed by particle diffusion. Adsorption thermodynamic studies revealed the adsorption processes to be endothermic, spontaneous and physical. The regeneration results revealed that the adsorbents were used successfully for five cycles of adsorption. Commercial activated carbon was also studied under same condition to compare the efficiency of the prepared adsorbents.

CHAPTER ONE

INTRODUCTION

1.0 Research overview

Presented in this chapter is an overview of the research background. The scope covers the current scenario on water pollution and problems of industrial effluents (mainly paper and textile) in Nigeria. The need to find more economical way of effectively solving the problem was described focusing on adsorption by activated carbons derived from agricultural by-products. Common factors affecting the preparation of activated carbons are also reviewed. The problem statement and the objectives of this research are also presented.

1.1 Water pollution and industrial effluents

Water is crucial to life, its availability is also essential for agriculture and ensures the sustainable increase of grain yield as well (Lu et al., 2015). Apart from drinking and agriculture, water is also the solvent used by nature in biological chemistry (Ma et al., 2015). Although the greater part of earth is surrounded by water, only a fraction of it is appropriate for drinking with only about one quarter of the world's population having access to hygienic drinking water according to world health organization (WHO) estimation, with the problem more pronounced in developing countries (Hamad et al., 2011).

Recently, one of the most troubling environmental challenges bedeviling several developing countries is water pollution; with numerous streams and rivers being polluted more often by natural and artificial activities. Water pollution contaminates streams, bays, lakes or oceans by hazardous substances that have direct effect on living species (Galadima et al., 2011).

Most of the customary sources for fresh water are revealed to be polluted in Nigeria, leading to fatal outbreak of diseases. As reported by previous researchers, about 19 % of the whole Nigerian population is affected, with some rural communities having up to 50 % occurrence (Umeh et al., 2004).

Significant consideration was given with regard to the recycle and reuse of wastewater as a result of the increasing water demand. Thousands of chemical contaminants have been found in the wastewater with many of them having organic origin (Annadurai et al., 2000). Chlorophenols belong to a class of those contaminants with organic origin, widely used in producing wood preservatives, biocides as well as pesticides (Bae et al., 2002).

1.1.1 Chlorophenols and their sources

Chlorophenols (CPs) are a group of organochlorides of phenol containing one or more covalently bonded chlorine atoms, which can be divided into five groups namely; mono-chlorophenols (2-CP, 3-CP, 4-CP), dichlorophenols (DCPs), trichlorophenols (TCPs), tetrachlophenols (TeCPs) and pentachlorophenols (PCPs) (Fan et al., 2015). They pose severe health hazard by affecting human nervous as well as respiratory systems. They also have strong odor, not readily biodegradable, persistent in the environment as well as toxic and carcinogenic features (Armenante et al., 1999; Tan et al., 2009). Sources of these compounds include waste water as a result of industrial activities such as pharmaceutical, petrochemical, plastic, wood preserving, pesticide, iron, steel, textile as well as paper industries (Fattahi et al., 2007; Hamad et al., 2010). Additional sources of chlorophenols in the environs are;

combustion of organic matters (Al-Thani et al., 2007), burning of urban waste (El-Sayed et al., 2009) as well as biodegradation of pesticides (Czaplicka, 2004).

Due to the increase in industrialization and agriculture in Nigeria, considerable amount of pollution to many rivers in the country also increased tremendously especially from textile and paper industries.

1.1.1.1 Paper Industrial Effluents

Paper and pulp mills are among the major sources of industrial pollution worldwide. Pulping is synonymous to the process of treating wood raw materials either chemically or mechanically in order to separate hemicelluloses and cellulose fiber and at same time improve paper quality. A large number of organic pollutants including chlorophenols that are very toxic and undesirable are present in waste waters generated from the pulp and paper mills (Lawrence & Yang, 2006). Brightening and whitening of the pulp (by removing residual lignin) involve different stages with bleaching among the processes employed. Toxicity arises from the bleaching process where chlorine and other chlorinated compounds are widely used (Sharma et al., 1996). Some chlorinated phenolic compounds like guaiacols, catechols, phenols and vanillin were identified in pulp mill bleaching effluents (Sharma & Kumar, 1999).

1.1.1.2 Textile industrial effluents

Another source of water pollution by chlorophenols and other toxic substances are textile industries; with Nigeria witnessing a considerable development in these industries. Phenolic compounds are common contaminants found in the water streams of textile industry. These hazardous wastes are also released by industries such as chemicals, petrochemicals, petroleum refineries, pharmaceuticals as well as phenolic resins (Gao & Wang, 2007). Presence of these phenolic compounds can be a hindrance to the use of water (Ioannidou & Zabaniotou, 2007) with them being mutagenic, carcinogenic and resistant to biodegradation (Wang & Zhu, 2007).

1.1.2 Properties of chlorophenols

With the exception of 2-chlorophenol, other chlorophenols are solids, with their water solubility decreasing with increase in the amount of chlorine atoms. Their acidity is weak, yielding salts that are highly soluble in water when reacted with alkaline metals such as sodium and potassium (Czaplicka, 2004). Some chlorophenols properties are described in Table 1.1.

1.1.3 Toxic effect of chlorophenols

Toxicity of chlorophenols is the extent to which they inhibit a chemical reaction or pollute water, land and/or air severely. The chlorophenols toxicity was influenced by the extent of chlorination as well as chlorine atoms location relative to the hydroxyl groups (Czaplicka, 2004).

It was reported that chlorophenols with chlorine atoms at the positions 2- or 2,6- relative to the hydroxyl group were less immune to microbial degradation than their isomers with chlorine atoms at positions 3- or 3,5- (Liu et al., 1982; Saito et al., 1991). Chlorophenols with the chlorine atom at the position 2- were also reported to be less toxic than other chlorophenols (Czaplicka, 2004).

Table 1.1 Physical–chemical properties of chlorophenols (Czaplicka, 2004)

Compound	**Formula**	**Molecular weight (g mol^{-1})**	**Boiling point (^{o}C)**	**Melting point (^{o}C)**	**Solubility (g L^{-1})^a**	**pKa**
2-Chlorophenol	C_6H_5ClO	128.56	174.9	93	28	8.3-8.6
3-Chlorophenol	C_6H_5ClO	128.56	214	33-34	26	8.8-9.1
4-Chlorophenol	C_6H_5ClO	128.56	217-219	42-44	27	9.1-9.4
2,3-Dichlorophenol	$C_6H_4Cl_2O$	163.00	206	57-58	Na	6.4-7.8
2,4-Dichlorophenol	$C_6H_4Cl_2O$	163.00	210	45	4.50	7.5-8.1
2,5-Dichlorophenol	$C_6H_4Cl_2O$	163.00	211	58-59	na	6.4-7.5
2,6-Dichlorophenol	$C_6H_4Cl_2O$	163.00	219	68	na	6.7-7.8
3,4-Dichlorophenol	$C_6H_4Cl_2O$	163.00	253-254	65-68	na	7.4-8.7
3,5-Dichlorophenol	$C_6H_4Cl_2O$	163.00	233	68	na	6.9-8.3
2,3,4-Tichlorophenol	$C_6H_3Cl_3O$	197.45	Sublimes	77-84	0.22	6.5-7.7
2,3,5-Tichlorophenol	$C_6H_3Cl_3O$	197.45	248-255	57-62	0.22	6.8-7.4
2,3,6-Tichlorophenol	$C_6H_3Cl_3O$	197.45	246	58	na	6.0-7.1
2,4,5-Tichlorophenol	$C_6H_3Cl_3O$	197.45	Sublimes	67-70	0.948	7.0-7.7
2,4,6-Tichlorophenol	$C_6H_3Cl_3O$	197.45	243-249	69	0.434	6.0-7.4
3,4,5-Tichlorophenol	$C_6H_3Cl_3O$	197.45	271-277	101	na	7.7-7.8
2,3,4,5-Tetrachlorophenol	$C_6H_2Cl_4O$	231.89	Sublimes	116-117	0.166	6.2-7.0
2,3,4,6-Tetrachlorophenol	$C_6H_2Cl_4O$	231.89	150	70	0.183	5.3-6.6
2,3,5,6-Tetrachlorophenol	$C_6H_2Cl_4O$	231.89	188	114-116	0.100	5.2-5.5

na, not available

[a] Solubility (g L^{-1}) at 20 ^{o}C.

1.1.4 Treatment of industrial effluents

The contamination of water by organic pollutants is a world-wide problem that still seeks an effective solution (Tomei et al., 2015). The development of effective treatment processes over a wide diversity of industrial wastewaters containing highly toxic chlorinated organic pollutants is gaining a growing interest (Puyol et al., 2015). Processes such as membrane separation (Amini et al., 2011), photo-Fenton degradation (Ayodele et al., 2012), sonochemical degradation (Abbasi & Asl, 2008), electrochemical degradation (Fan et al., 2008), coagulation, among others have been applied, but adsorption on activated carbon surpassed all of them as the best process in wastewater treatment due to its simplicity in design and applicability, fast adsorption kinetics, effectiveness and universal nature (Ali et al., 2012). It can be applied to remove both soluble and insoluble organic pollutants with about 99.9% efficiency but the high price of commercial activated carbon calls for search to alternatives or substitutes for the adsorbent (Al-Degs et al., 2009).

Nigeria and many parts of the world are blessed with abundance of minerals and organic resources that are lying fallow and most often regarded and disposed off as wastes (El-Hendawy, 2005). These include agricultural and industrial byproducts; research has shown that these agricultural wastes have the potentials to be transformed into good and useful adsorbents for effective wastewater treatment (Halim et al., 2012).

Adsorption process though predominantly a physical process has often exhibited chemisorptions capability, depending on the forces involved. Physical adsorption is non-specific (any adsorbate-adsorbent interaction) and takes place at enthalpy between 10 to 20 kJ mol^{-1} while specific chemisorptions occurs between enthalpy of 40 to 400 kJ mol^{-1} (Kołodyńska et al., 2012; Saha et al., 2010). Adsorption process is effective, easy to use, and its treated wastewater is reusable but the expensive commercial activated carbon used as adsorbent is its major disadvantage.

Activated carbon is majorly an amorphous (with little microcrystalline structure) carbon material exhibiting high porosity and extended internal surface area. It can be prepared by either physical or chemical activation (or both) through pyrolysis of carbonaceous material in an inert atmosphere. The preparation entails elimination of non-carbon materials such as sulfur, hydrogen, oxygen and nitrogen as vapor leaving mainly carbon atoms; before the completion of the activation process, the rearranged carbon atoms are developed into porous material with high and extended surface area (Rambabu et al., 2013). Activated carbons are obtained mainly in powder (small internal surface area) and granular (larger internal surface area) forms; which are associated with large and smaller pores, respectively. It has wide applicability which includes its use in wastewater treatment, pharmaceutical industries, paper and pulp mill, automobile industries, hydrometallurgy, medicine, food and oil industries.

Despite their prolific use, certain problems with the high costs of commercial activated carbons have limited their applications. The high production cost is largely due to non-renewability and expensiveness of the starting materials such as bituminous coal, lignite and petroleum coke which prompted increasing research interest in utilizing low cost materials such as agricultural and industrial byproducts for the production of activated carbons.

1.2 Wastewater treatment methods

Water pollution irrespective of the source (ocean, lakes, rivers and underground reservoirs) is caused by the presence of chemicals, particulate or bacterial matter that degrades its purity and quality limiting the availability of pure water for agricultural, domestic, industrial, public and other uses; therefore, protecting clean surface water has become a security issue as it is imperative for the custodian of natural resources (Cheng & Jia, 2010; Werner et al., 2012).

Since no particular technique is universally suitable in all pollutant removal, it is therefore crucial to understand the wastewater source, typical wastewater composition and the process of generating the waste within the facility so as to know the pretreatment ramifications as well as the method that will be suitable (Ali et al., 2012).

Biological, chemical and physical are among the numerous techniques engaged for the removal of contaminants from wastewaters (Ghoreishi & Haghighi, 2003).

1.2.1 Biological Method

This technique has long been employed in the chemical industries for wastewater treatment with bacteria and some microorganisms being employed for biological treatments through assimilation to remove pollutants. These bacteria have ability to provide the required energy needed for microbial metabolism and building block for cell synthesis through the use of diverse wastewater constituents. Through this metabolic activity, pollutants are removed as by products, raw materials for the metabolism and as generated products in chemical processing industries. This technique requires low capital and operating costs when compared with chemical and physical techniques, degrades or destroys organic pollutants and reduces aquatic toxicity. However, the method is not flexible in operation and design, may require large areas of land for the operation (Fayidh et al., 2011) and anaerobic breakdown yields methane and hydrogen sulphide.

1.2.2 Chemical method

Chemical treatment methods improve water quality through reactions which require certain chemicals (Sabur et al., 2012). Some of the chemical treatment processes include coagulation, flocculation, ozonation and electrochemical destruction which are very effective in treating many industrial wastewaters but might generate waste (sludge) which will further pose a disposal problem. The need for some chemical reagents (chlorine, aluminum sulfate-alum, lime etc.) and energy for the reaction often incur costs in the process which makes it unattractive (Hassan et al., 2009).

1.2.3 Physical method

Physical method of wastewater treatment consists of processes that do not require rigorous biological or chemical changes but predominantly physical phenomena to upgrade wastewater quality. Adsorption by activated carbon, membrane filtration, ion exchange, irradiation and electrokinetic coagulation are some of the physical treatment methods with adsorption being the most superior compared to other methods because of its cheapness, high efficiency, simplicity in design, ability to treat pollutants in more concentrated form and ease of operation (Anbia et al., 2010 ; Li et al., 2011a). Another advantage of adsorption is, it does not lead to the formation of toxic substances (Crini, 2006). Adsorption process became a major industrial separation technique due to the advent of cheaper, effective and efficient precursors that can serve as an option to the high price of commercial activated carbon (Crini, 2006).

1.3. Adsorption

The accumulation of material at the boundary between two phases (gas–solid or liquid–solid boundary) is referred to as adsorption. Adsorbate is the material that accumulates at the interface while the solid on which adsorption takes place is termed as adsorbent (Dabrowski, 2001). Two key forms of adsorption are physical and chemical. Chemical adsorption or chemisorption is mainly described by being irreversible as well as the development of a strong chemical connections between adsorbates ions or molecules to the surface of adsorbent, which is mainly due to swapping of electrons, physical adsorption or physisorption on the other hand is characterized by being reversible in most cases as well as weaker van der Waals bond between adsorbent and adsorbate (Allen & Koumanova, 2005).

pH as well as ionic strength are among the key factors impacting the phenolic compounds adsorption. At lower pH, the uptake of phenolic compounds by different adsorbents is intensified due to the phenols being undissociated (Caqueret et al., 2008; Dargaville et al., 1996; García-Araya et al., 2003; Grant & King, 1990; Mohan & Karthikeyan, 1997). Hydrogen may play an important role (Bretag et al., 2009; Chanda et al., 1983; Grohmann et al., 1999; Kammerer et al., 2010a; Ku & Lee, 2000; Liu et al., 2010a; Navarro et al., 2008; Pompeu et al., 2010). Adsorption decreases at higher pH due to occurrence of hydroxyl and carboxyl groups dissociation (Fu et al., 2005; Yoon et al., 1997). Adsorbate characteristics also have impact on adsorption (Brune et al., 1999; Cheng et al., 2006; Geng et al., 2009; Li et al., 2009; Pan et al., 2005).

1.3.1 Activated carbon

An amorphous high porous carbonaceous material is generally termed as activated carbon. Its materials are very well known for their versatile surface characteristics with an extended inter particulate surface area, possessing small hydrophobic graphite layers (María et al., 2011) thus making it useful for both adsorption and catalytic applications (Bansal & Goyal, 2005; Kazmierczak-Razna et al., 2015). Activated carbon is prepared by partial combustion or pyrolysis of carbonaceous materials (wood, coal char, almond, coconut, or walnut shells etc.). To date, it has been the most prevalent adsorbent material (Li et al., 2015) with popular applications in industrial and wastewater treatment (Bhatnagar & Sillanpää, 2010; Cheng et al., 2015), air pollution remediation (Chen et al., 2012), pharmaceuticals (Delgado et al., 2012), oil and gas industry (Ali et al., 2012) and food processing (Nasehi et al., 2012). Powder and granular are the two most common and widely used physical forms of activated carbon. Fiber is another form that is attracting increasing attention, mostly attained from petroleum pitch, isotropic coal as well as cloths (Rodriguez-Reinoso et al., 1995).

1.3.1.1 Demand for activated carbon

As at 2003, the global consumption of activated carbon was put at 350,000 tons with an estimated rise of 7 % annually (Maroto-Valer et al., 2003). An estimated 600,000 tons was predicted to be in demand for consumption in the year 2015 based on that yearly 7 % annual rise in consumption. This rapid rise in world demand reflects the enormous increase in the applications found for activated carbon. The demand is also on the increase in developing countries like Nigeria. In Ghana for instance, about 4,681,866 kg of activated carbon valued at 12,706,290,390 c was imported for use between 1992 and 1997 (Lartey & Acquah, 1999). There are strong indications that Nigeria, South Africa and a few other African countries have statistic of importation similar to Ghana if not more because of the several industries in those places that require the use of ACs.

1.3.1.2 Raw materials availability in Nigeria

Nigeria is one country blessed with abundant human, mineral and agricultural resources. The country is rich in oil but before the advent of oil, the economy was being sustained by agriculture. Among the agricultural produce is *Prosopis africana*. Others include palm kernel, cocoa, cotton, rubber and groundnuts being produced all over the country. Presently, the use of agricultural by-products for activated carbon production has been noticed by many researchers (Yahya et al., 2015) for adsorption of heavy metals and other contaminants. *Prosopis africana* is one of the many agricultural by-products that are very abundant in Nigeria and other Savannah regions of West Africa.

1.3.1.3 Precursors for activated carbon

Almost all the precursors that can be used for the ACs preparation are carbonaceous materials. Features of some materials and the type of ACs usually produced from them are shown in Table 1.2.

Table 1.2 Properties of some raw materials used in ACs preparation (Streat et al., 1995)

Raw material	**Carbon (mass %)**	**Volatiles (mass %)**	**Density ($cm^3 g^{-1}$)**	**Ash (mass %)**	**Texture of activated carbon**
Soft wood	40-45	55-60	0.4-0.5	0.3-1.1	Soft, large pore volume
Hard wood	40-42	55-60	0.55-0.8	0.3-1.2	Soft, large pore volume
Lignin	35-40	58-60	0.3-0.4	-	Soft, large pore volume
Nutshells	40-45	55-60	1.40	-	Hard, large micropore volume
Lignite	55-70	25-40	1.0-1.35	5-6	Hard, small pore volume
Soft coal	65-80	20-30	1.25-1.5	2-12	Medium hard, medium pore volume
Petroleum coke	70-85	15-20	1.35	0.5-0.7	Medium hard, medium pore volume
Semi-hard coal	70-75	10-15	1.45	5-15	Hard, large pore volume
Hard coal	85-95	5-15	1.5-1.8	2-15	Hard, large pore volume

Since carbon is the major component of activated carbon, the fixed carbon content, volatile component and ash content of the material are of great importance; also the carbon material should have high abrasion resistance, non hazardous, cheap and readily available. The nature of the carbon material determines the type of activated carbon produced (Kılıç et al., 2012). The seed hulls of *Prosopis africana* were revealed to have high carbon and low inorganic contents qualifying it to be a good precursor for AC preparation as adsorbent.

Commercial activated carbons are mostly expensive due to high cost and non-renewable starting materials such as bituminous coal, lignite and petroleum coke (Gao et al., 2015). To augment for those shortcomings, other potential raw-materials that are renewable and of commercial capability have been found and utilized as precursors for AC production as shown in Table 1.3.

Table 1.3 Agricultural wastes employed to prepare low cost adsorbents

Precursor	**Reference**
Date Pits	(Akhrib et al., 2013; Awwad et al., 2013)
Coconut husk and shell	(Babarinde, 2002; Bello & Ahmad, 2012; Cazetta et al., 2013; Cosnier et al., 2006; Foo & Hameed, 2012a; Kulkarni et al., 2013; Tan et al., 2008)
Hazelnut shell	(Demirbas et al., 2002; Doğan et al., 2009)
Rice husk and straw	(Bishnoi et al., 2003; Chen et al., 2013; Lin et al., 2013; Verma & Mishra, 2010; Wang et al., 2007)
Apricot stone	(Abbas et al., 2014; Soleimani & Kaghazchi, 2008)
Harmal seeds residue	(Tofighy & Toraj, 2014)
Olive stone and pits	(Alslaibi et al., 2013; Bohli et al., 2015; Redondo et al., 2015; Soudani et al., 2013)
Sour cherry stones	(Angin, 2014)
Almond shell	(Izquierdo et al., 2011; Omri et al., 2013)
Loosestrife	(Fan et al., 2011)
Nipa palm nut	(Nwabanne & Igbokwe, 2011)
Jatropha seed coat	(Hirunpraditkoon et al., 2015)
Bamboo	(Hameed et al., 2007; Prangtead, 2011)
Tea waste	(Ali et al., 2013; Auta & Hameed, 2011)
Coffee extract residue	(Tehrani et al., 2015)

1.3.1.4 Activated carbon preparation

The precursor nature, activation method employed as well as the extent of activation played a big role in the porosity of ACs (Dabrowski et al., 2005). Generally, two main stages are involved during the AC preparation, they are carbonization and activation processes. The method is started with carbonization, aimed at lessening the lignocellulosic precursors of impurities by volatilizing the non-carbonaceous portion in a specifically designed furnace, at temperature usually lower than 800 ^{o}C without oxygen so as to enhance the quality of the resulting char (Cagnon et al., 2009; Daud et al., 2003; Lua et al., 2006; Sun & Jiang, 2010; Tsai et al., 1998). After carbonization, the next process is activation; Activation process refers to the preparation of the active site by the use of a gas such as CO_2 in order to develop the ACs pore volume as well as its surface area.

Carbonization

This involves removal of moisture content, volatile organic materials (alcohols, carboxylic acid, and phenol) or non carbon elements like sulfur, nitrogen, oxygen and hydrogen from the precursor through pyrolysis in an atmosphere that is static. Heating of the furnace may be controlled for higher yield and better quality of char produced; from room temperature to 200 ^{o}C, then to 400-500 ^{o}C (Lozano-Castelló et al., 2001; Wereko-Brobby & Hagan, 1996; Yuen & Hameed, 2009). The resulting char undergoes irregular arrangement of its residual aromatic sheets resulting to interstices between the carbon materials (Bansal & Goyal, 2005). In order to obtain low volatilization and a high char yield, low heating rates (10–15 ^{o}C min^{-1}) are used. Char has a high fixed carbon content which is important for producing activated carbon (Norhusna et al., 2013). Lower heating rate will increase dehydration and improve the stabilization of the polymeric components (Ioannidou & Zabaniotou, 2007; Suhas et al., 2007). However, the microporosity of char has been found to be independent of the precursor composition and the carbonization heating rate (Suhas et al., 2007).

Activation

The activation process is about enhancing the pore volume, enlarging the diameter of pores and increasing the porosity of activated carbon (Norhusna et al., 2013). It involves the conversion of carbon materials (char) into porous substance with increased surface area by clearing the char pore blockages through a gasification process with carbon dioxide or steam as activating agents or their mixture. The temperature of the gasification usually ranges from 800-1200 ^oC depending on the precursor used (Crini, 2006; Gupta & Suhas, 2009; Rambabu et al., 2013). Activation process can be physical, chemical or physiochemical (a combination of physical and chemical activation).

Physical activation constitute partial gasification of char (resulting from raw material carbonization in a static atmosphere) with steam, CO_2 or their mixture (Rodriguez-Reinoso et al., 1995). During physical activation, the oxidizing agents react with the carbon materials, which is favorable at a very high temperature (>900 ^oC) (Yuen & Hameed, 2009). The process is environmentally benign due to non production of waste products since gaseous agents are used, although the process is slow with high energy demand and carbon yield (Arami-Niya et al., 2011). For physical activation, steam is more effective than CO_2, because activated carbon with a relatively higher surface area can be produced (Norhusna et al., 2013). The smaller molecule size of water is responsible in effectively facilitating diffusion within the char's porous structure (Cagnon et al., 2009; Mak et al., 2009). Steam activation is also reported to be two or three times faster than CO_2 at the same degree of conversion (Nowicki et al., 2010; Plaza et al., 2010).

But when the precursor is permeated or impregnated with a chemical compound, it is referred to as chemical activation; the permeated product is then pyrolysed and later washed with distilled water in order to get rid of the activating agent. H_3PO_4, KOH, NaOH, K_2CO_3 and $ZnCl_2$ are some of the most popular activating agents (Yahya et al., 2015). These chemical agents develop the porosity and inhibit tar formation through their influence on decomposition as they serve as dehydrating agents (Dabrowski et al., 2005; Norhusna et al., 2013). Generally, chemical activation (300–500 ^{o}C) takes place at lower temperature than physical activation (Bhadusha & Ananthabaskaran, 2011; Sayan, 2006; Sumathi et al., 2010). This improves the development of pore in carbon structure due to the effect of chemical agent (Sudaryanto et al., 2006).

The chemical activation process produces an excellent rigid matrix carbon adsorbent (not easily volatilized or contracted) material at lower temperature than physical activation (Deng et al., 2009). The yield of physical activation is usually lower than that of chemical activation process by up to about 30 % (Dabrowski et al., 2005). Other merits of chemical activation process in comparison to physical activation include easiness (as there no need of carbonizing the precursor), lesser activation temperatures as well as superiority in porosity development (Dabrowski et al., 2005).

In the case of physico-chemical activation process, both physical together with chemical activation processes are concurrently run together. Therefore, oxidizing agents (CO_2, steam, air or their mixture) and dehydrating agents (NaOH or KOH or K_2CO_3 etc) are used for porosity and surface area development through gasification in a temperature range of 600-850 (±1) ^{o}C (Arami-Niya et al., 2011). This dual advantage of having two processes incorporated as one is producing high quality activated carbon with low ash content, high porosity and surface area (Azevedo et al., 2007)

Quite a number of researches have been carried out using these three methods for ACs production; Table 1.4 presents a brief summary of such methods.

1.3.2 Optimization of activated carbon preparation conditions

Proficient and effective adsorbents are prepared with the aid of experimental design which helps in reducing cost of design and labor, achieving optimal output, identifying the significant factors (input), improving process or product robustness, reducing variability and minimizing process variation (Dutta et al., 2011; Gómez Pacheco et al., 2012). The experimental design comprises of the factors (process input), levels (the settings or magnitude of individual factor to be studied) and the response (expected experimental output).

Response surface methodology (RSM) is the statistical technique that has been used by many researchers to determine equations of regression model under certain operating conditions (Ahmad & Alrozi, 2010a; Auta & Hameed, 2011). It involves using statistical techniques to model and analyze experiments that are influenced by many variables towards achieving a set goal or response. The RSM comprises of design methods like box-behnken, 3-level factorial, central composite, hybrid, pentagonal, hexagonal, D-optima, distance-based, modified distance, user deformed and historical data.

Table 1.4 Physical, chemical and physico-chemical methods of preparing activated carbons

Method of activation	**Raw Materials**	**Agents used**	**Reference**
Physical activation	Durian peel	CO_2	(Nuithitikul et al., 2010)
	Almond shell	CO_2	(Marcilla et al., 2000)
	Rubber-seed shell	Steam	(Sun & Jiang, 2010)
	Coconut shell	Steam	(Cosnier et al., 2006)
Chemical activation	Durian shell	KOH	(Chandra et al., 2007)
	Plum stones	KOH	(Nowicki et al., 2010)
	Corn cob	$ZnCl_2$	(Tsai et al., 1998)
	Euphorbia rigida	$ZnCl_2$, K_2CO_3, NaOH, H_3PO_4	(Kılıç et al., 2012)
Physico-chemical activation	Pistachio nut shell	KOH, Steam,	(Yang & Lua, 2003)
	Fluid petroleum coke	KOH, H_3PO_4, Steam, CO_2	(Rambabu et al., 2013)
	Pistachio nut shell	NaOH, CO_2	(Lua & Yang, 2009)
	Palm shell	NaOH, CO_2	(Hamad et al., 2010)
	Walnut shell	KOH, CO_2	(Plaza et al., 2010)

Among the RSM subsets, central composite design (CCD) technique is the most widely used second-order model by scientists and engineers due to its suitability in analyzing interaction between preparation parameters as well as validating a quadratic surface (Ahmad & Alrozi, 2010a). It also requires the least quantity of experimental trials to optimize the parameters influence, either singly or through parameters interaction (Auta & Hameed, 2011). 2n axial, 2^n factorial and six center runs (n_c) comprises the CCD, with the amount of factors denoted as n. The total number of experiments can be evaluated using equation (1.1):

$$\text{Total number of experiments} = 2n + 2^n + n_c \tag{1.1}$$

Experimental error and data reproducibility can be determined using center points with +1 and -1 representing two-level independent variables for maximum and minimum values respectively, representing the eight factorial points. The six replicates location is at the center (0, 0, 0) and (±α, 0,0), (0, ±α, 0) and (0,0, ±α) were describing the axial points. The distance of the axial point from center is represented by alpha (α), taken as α=1. 682. It can be obtained using equation 1.2 below (Auta & Hameed, 2011):

$$\alpha = N_p^{1/4} \tag{1.2}$$

where number of points in the cube portion of the design is described by $N_p=2^k$ while k is the variables amount. The prime response or output function for the single and multiple effects of the factors involved either separately or through interaction between them is expressed as:

$$Y = b_o + \sum_{i=1}^{n} b_{ii}x_i \; + \left(\sum_{i=1}^{n} b_{ii}x_i\right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij}x_ix_j \tag{1.3}$$

where Y is the response predicted, b_o stands for the constant coefficients-experimental error (measurement error on the response and unaccounted variations), b_{ii} and b_{ij} are the quadratic as well as the interaction coefficients respectively. The variables coded values are x_i and x_j.

Design Expert software can be applied to assess the model fitting and statistical analysis in order to fit response function developed as well as evaluate statistical significance of the function. Significance and adequacy of the CCD quadratic models generated is carried out using F-test method of analysis of variance (ANOVA). Response surface methodology has been applied by researchers in the preparation of activated carbons, a brief summary of such studies are presented in Table 1.5.

Table 1.5 Optimum parameters for activated carbon preparation using response surface methodology

Activated carbon precursor	Parameters optimized	Reference
Borassus aethiopum shells	780 ^oC, 1.05 h, 3.19 IR	(Garba et al., 2014)
Biological sludge	700 ^oC, 3 h, 0.5 IR	(Gómez Pacheco et al., 2012)
Mangosteen peel	828 ^oC, 1 h, 3.0 IR	(Ahmad & Alrozi, 2010a)
Date stone	707 ^oC, 1.27 h, 1.6 IR	(Theydan & Ahmed, 2012)
Palm oil fronds	750 ^oC, 2 h, 2.38 IR	(Salman, 2014)
Oil palm empty fruit bunch	814 ^oC, 1.9 h, 2.8 IR	(Hameed et al., 2009)
Tea waste	800 ^oC, 2 h, 1.4 IR	(Auta & Hameed, 2011)

1.4 Adsorption isotherm

Isotherms are functions relating the adsorbate amount on the adsorbent with its pressure in the case of gas or its concentration if liquid at fixed temperature. It can be used to study and explain the whole adsorption and desorption processes. A clue of the nature of adsorption process is gained by inspecting the isotherm shape. Based on the Brunauer-Emmett-Teller (BET) classification, all adsorption isotherms fit into one of the five (5) types shown in Figure 1.1. Characteristics of the isotherm types are listed below.

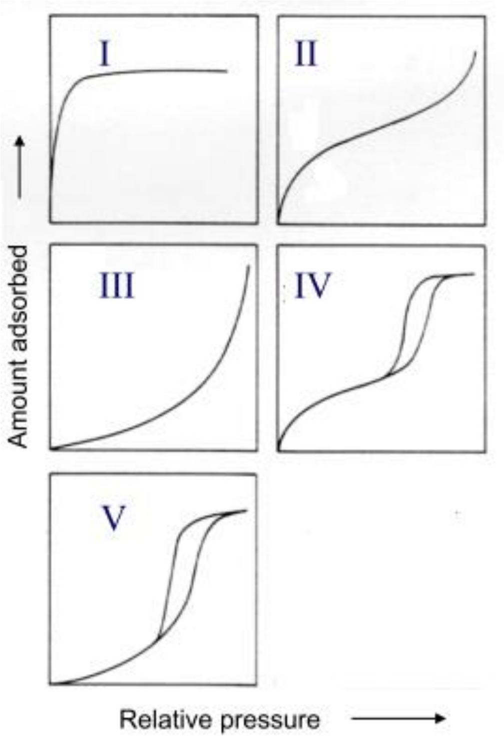

Fig 1.1 Diagrammatic representation of isotherm classification (Sing et al., 1985).

Type I happened when adsorption is restricted to monolayer as observed in chemisorption. Pores are indicated to be microporous by the physical type of adsorption that generates the Type I isotherm with the uncovered surface located almost solely inside the micropores, which once packed with adsorbates, leave little or no external surface for additional adsorption.

Type II is encountered more recurrently when adsorption takes place on adsorbents that are nonporous or adsorbent with pore diameter larger than micropores. The inflection point normally happens near the completion of the first adsorbed monolayer and with upsurge in relative pressure.

Type III isotherms are principally illustrated by heat of adsorption that is less than adsorbate heat of liquefaction. Thus, as adsorption proceeds, interaction with an adsorbed layer is greater than the interaction with adsorbent surface.

Type IV occurs on adsorbents that are porous, having pores in the range of 1.5-100 nm. The slope shows increased uptake of adsorbate as pores become filled, at higher pressures. The inflection point normally occurs near completion of the first monolayer.

Type V occurs as a result of interaction between adsorbate and adsorbent potential similar to the type III at low pressure. However, Type V is also related with pores in the range as those of Type IV isotherm.

Generally, Type I, IV and V are associated with porosity, while Type I usually corresponds to micro porosity, Type IV and V are associated with pores ranging from about 1.5 to 100 nm. Each of these types is observed in practice but by far the most common are Type I, II and IV (Thomas & Crittenden, 1998).

Isotherm models gave an indication on how the interaction between adsorbent-adsorbate occurs. Three most relevant models applied in this work are Langmuir isotherm, Freundlich isotherm and Temkin isotherm equations.

1.4.1. Langmuir adsorption isotherm

Langmuir isotherm equation describes an adsorption process that occurs upon a homogeneous surface where the adsorbate is distributed in monolayers (Kumar et al., 2010). The model is given as (Langmuir, 1916):

$$q_e = \frac{K_L Q_a^0 C_e}{1 + K_L C_e} \tag{1.4}$$

where q_e stand for the adsorbate amount adsorbed per unit adsorbent weight, Q_a^0 (mg g^{-1}) and K_L (L mg^{-1}) are maximum monolayer adsorption capacity and is Langmuir equilibrium constant, respectively. Five linear forms can be derived from equation 1.4 as presented in Table 1.6, with their main differences linked to the spreading of data and subsequently to the correctness in determining the parameters (Baccar et al., 2013).

Table 1.6 Linear forms of Langmuir isotherm

Isotherm	**Linear form**	Plot
Langmuir-1	$\frac{1}{q_e} = \frac{1}{K_L Q_a^o C_e} + \frac{1}{Q_a^o}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$
Langmuir-2	$\frac{C_e}{q_e} = \frac{C_e}{Q_a^o} + \frac{1}{K_L Q_a^o}$	$\frac{C_e}{q_e}$ vs C_e
Langmuir-3	$q_e = -\frac{q_e}{K_L C_e} + Q_a^o$	q_e vs $\frac{q_e}{C_e}$
Langmuir-4	$\frac{q_e}{C_e} = -K_L q_e + K_L Q_a^o$	$\frac{q_e}{C_e}$ vs q_e
Langmuir-5	$\frac{1}{C_e} = \frac{K_L Q_a^o}{q_e} - K_L$	$\frac{1}{C_e}$ vs $\frac{1}{q_e}$

The dimensionless separation factor (R_L) described the fundamental characteristics of Langmuir equation, defined as (Baccar et al., 2013):

$$R_L = \frac{1}{1 + K_L C_o} \tag{1.5}$$

with C_o (mg L^{-1}) being the highest initial concentration. The range of R_L values hint at whether the adsorption is not favored ($R_L > 1$), straight ($R_L = 1$), favored ($0 < R_L < 1$), or not reversible ($R_L = 0$) (Hamad et al., 2010).