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Comparative Adsorption and Kinetic studies on Batch column Treatment of Wastewater using Unactivated and activated Cherry Seed Carbon (*Chrysophyllum albibum)*

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Abstract
Wastewater from fishery was treated using unactivated and activated carbon from Cherry seed shell, one part of the material was activated with 50% saturated ammonium chloride solution and the other unactivated. The substrates were carbonized in a muffle furnace at 500^oC for three hours. The powdered unactivated and activated carbon obtained were characterized in terms of pH, bulk density, surface area, negative surface charge, moisture content, volatile matter content and ash content. The result of the powdered unactivated carbon characterized was pH 8.70 ±0.02, bulk density, 0.79 ±0.01g/cm^3, surface area, 0.057 ±0.01g/mgI_2 negative surface charge, 1.77 ±0.01mmol/H+, moisture content, 9.82 ±0.00% volatile matter, 0.05 ±0.00%, ash content, 0.12 ±0.00%. and the activated carbon was pH 7.20 ±0.01, bulk density, 0.80 ±0.02g/cm^3, surface area, 0.17 ±0.03g/mgI_2, negative surface charge, 1.92 ±0.03mmol/H+, moisture content, 2.65 ±0.00% volatile matter, 47.50 ±0.00%, ash content, 7.50±0.00%. The wastewater was characterized for its pollution characteristics, Temperature, 29.60±0.00^{O}C, alkalinity,115.90±2.00mg/L turbidity, 178.47±2.00NTU,pH 6.92, conductivity; 633±3.00µs/cm, total suspended solid, 498.00±3.00mg/L, total dissolved solid 302.00±2.00 mg/L. nitrate nitrogen, 13.86±0.01mg/L, ammonium nitrogen 79.75±1.00mg/L, sulphate 7.59±0.01mg/L, phosphate 4.28±0.00mg/L, dissolved Oxygen 0.00mg/L, chemical oxygen demand (COD) 184.00±2.00mg/L. biochemical oxygen demand (BOD) 158.60±2.00mg/L, Pb, 0.56±0.00mg/L, Zn, 1.50±0.00mg/L, Cd, 0.17±0.00mg/L, Cu 0.94±0.00mg/L. These values were high when compared with Federal Ministry of Environment and Standards (FMES) effluent discharged. The adsorption studies of the treatment fitted well into the Langmuir and Freundlich isotherms for both carbons. The adsorption kinetics was better described by pseudo-second –order for both carbons. The results revealed that powdered carbon from agricultural residue is efficient in the treatment of wastewater.

Keywords: *adsorption, kinetics, wastewater, unactivated, activated.*

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I. Introduction

Industrial wastes and agricultural by-products are classes of materials evaluated as promising precursors for the production of low-cost adsorbents, because they are renewable, locally available in large quantities and inexpensive (Alves, et. al 2013).

Wastewater treatment by adsorption using activated carbons (AC) is quite very effective and has been cited by EPA as being one of the best available environmental control technologies (Ahmedna, et. al 1997). However, the widespread use of AC adsorption is still restricted because of the high costs of commercial carbons. Thus, many recent studies have focused on the use of renewable and cheaper precursors, mainly agricultural wastes and by-products, as raw materials in the production of activated carbons (Oliveira, and Franca, 2011, Alves, et. al 2013). The basic processes of turning lignocelluloses materials (e.g. agricultural wastes and by- products) into an activated carbon can be divided into physical or chemical activation. Physical activation consists of heat treatment of the material in a stream of gases, usually carried out in a two –step process: (i) carbonization in inert atmosphere to produce the charcoal, followed by (ii) activation or a second heat treatment in the presence of CO_2 or steam to increase the porosity of the material (Oliveira, and Franca, 2011). Chemical activation is carried out by means of the impregnation of the carbon structure with an activating agent (either an acid or base) followed by heat treatment, so both the carbonization and activation steps are carried out simultaneously. This process is considered to be more advantageous in comparison to physical activation, because usually occurs at lower temperatures, leads to higher carbon yields, and allows better control of the development of microporosity.

Acid activation is generally employed in order to oxidize the porous carbon surface. It increases the acidic characteristic, removes the mineral elements, organic materials thereby improving the hydrophilic nature of surface (Bhatnagar, et. al 2013). In this report, Cherry seed shell was selected as precursor material and one part was activated with NH_4Cl and the other part was unactivated. To the knowledge of the authors there are no reports of previous attempt to produce activated carbon from Cherry seed shells .Cherry (Chrysophyllum albidum) is a tropical edible fruit tree. It belongs to the family sapotaceae which has up to 800 species and make up almost half the order Ebernales (Ehiagbonare, et. al 2008). It is primarily a forest tree species. The utilization of cherry seed shell in the production of activated carbon is of interest from both economic and environmental view points. It converts unwanted low-cost agricultural residue to useful high value adsorbent, which are increasing in use in adsorption in water and waste water treatment

Thus, the objective of this study was to evaluate the feasibility of using activated and unactivated carbon from locally and cheap agricultural waste as adsorbent in the treatment of wastewater using batch treatment

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II. Materials and Methods

Preparation and Characterization of Activated unactivated carbon from Cherry Seed Shells.

Cherry seed shells were obtained from Igueben, Edo State, Nigeria. About 1.0kg of the agricultural residues (Cherry Seed Shell) was steeped in the solution of the activating agent for a period of 24h at room temperature and the other part was unactivated. The mixture of the activated one was filtered and air-dried and both were then carbonized at 500^{oC} for 3hrs in a muffle furnace. The carbons were then ground into fine powder and sieved with the aid of 500mcs sieve and stored in dried sample bottles for use. The powdered activated and unactivated carbons prepared from Cherry seed shell were characterized in terms of pH, bulk density, (Ahmedna, et. al 1997), surface area, (Okieimen, et. al 1991), and surface charge (Toles, et. al 2000) moisture content, volatile matter content and Ash content. The detailed experimental procedures for the characterization of activated and unactivated carbons were given in a previous publication.

Optimum Dosage Determination of the Carbons

This study was done to determine the quantity(amount) of carbon (substrate) that would be suitable for treatment , 5.00g, 10.00g, 15.00g, 20.00g, 25.00g, 30.00g and 35.00g each of both the activated and unactivated carbons were added to 100ml of the wastewater respectively, the mixture was allowed to stand for one hour,. The mixture was filtered and the COD was determined. The percentage COD reduction was then calculated.

Treatment Methods: A cylindrical column was packed with the powdered carbon by placing a glass wool at the bottom of the column and the activated carbon was used to pack the column which was tightly packed to avoid any air space. 1,500mL of the waste water was allowed to flow through from an overhead plastic container. At the out let (batch) the effluent was collected at 10Minutes, 30Minutes, 50Minutes, 70Minutes, 90Minutes, 110Minutes and the physicochemical characterization was determined. The treated values obtained were then fitted in Adsorption isotherm of Langmuir, Freundlich, Adsorption models.

PHYSICOCHEMICAL CHARACTERIZATION OF CARBONS FROM CHERRY SEED SHELLS

Table 1.0: The results obtained from the Characterization of Carbons from Unactivated and Activated Cherry Seed shells

	pH	Bulk density g/ml	Surface area $mg/I_2/g$	Negative Surface charge	Moisture Content%	Volatile content	Ash content%
Cherry seed shell unactivated.	8.70±0.02	0.79±0.01	0.057±0.01	1.77±0.01	9.82±.00	0.05±0.00	0.12±0.00
Cherry seed shell 50% NH_4Cl Activated	7.20±0.01	0.80±0.02	0.170±0.03	1.92±0.03	2.65±0.00	47.50±0.00	7.50±0.00

III. Results and Discussion.

Table 1.0: Shows the Characterization of the Unactivated and activated carbons from Cherry seed shells. The values of pH of the carbons are 8.70 for unactivated cherry seed, 7.20 for Activated cherry seed. These pH values of carbon prepared are within the generally acceptable range of pH(6-8) in many applications , carbons with extreme pH values are capable of increasing or pH of slurry to points of optimum metal adsorption and or induce desirable physical/chemical changes (Bernardin, 1985, Ahmedna, et. al 2000).

In this study, the values of bulk densities of these carbons are for Unactivated Cherry seed 0.79 g/cm^3, Activated cherry seed 0.80 g/cm^3, these values are well within the acceptable range for powdered activated

carbon in many application whose rage is always within (0.5-0.6g/cm^3) (Carpenter, 1985, Ahmedna, et. al 2000).

Surface Area: The Surface area from this study are Unactivated cherry seed 0.057 mgI_2/g, and Activated cherry seed 0.170mgI_2/g, an indication that they are fairly good surface area. The surface area of this carbon obtained from cherry seed shells was determined by the iodine adsorption method which is a widely used routine procedure for the determination of surface area of powder. Large surface area is a requirement for good adsorbent. Surface area is the single most important characteristic of activated carbons designed for adsorption of compounds from liquid media. Report of previous studies (Okieimen, et. al 1991) that attempted to correlate surface area measurements by different methods suggest that the value of surface area which is an inverse of iodine number obtained for these carbons 0.057 mgI_2/g, and 0.170 mgI_2/g an indication that the unactivated carbon has a fairly low surface area. This surface area obtained is comparable with those reported for rubber seed shell Carbon (Okieimen, et. al 2005) rice husk carbon (Okieimen, et. al 2005) and cassava peel carbon (Ewansiha, et. al 2005). Ordinarily, raw charcoal has small adsorption capability because its surface area is small and the pores are largely filled with products of incomplete combustion. Activation involves distilling out of hydrocarbon impurities from a charcoal and this leads to exposure of a larger free surface for possible adsorption (Ewansiha, et. al 2005).The micro pores are created during activation process and are responsible for the larger surface area of activated carbon particles. Adsorption largely takes place in the micro pores. The type and net charge of functional group bonded to the carbon influence its surface characteristics and greatly affects the adsorption behaviour of activated carbons particles.

Surface charge: The adsorption capacity of activated carbons is determine by its porous structure and surface area but is also strongly influenced by the presence of functional groups at the surface. Activated carbons are known to contain a variety of hetero atoms such as oxygen, hydrogen, chlorine and sulphur. Heteroatom's are either derived from the starting material, and become a part of the chemical structure as a result of imperfect carbonization, or chemically bonded to the carbon during activation or during subsequent additional treatments, such as oxidation. These heteroatoms are bound to the edges of the carbon layers and form surface groups that greatly affect the adsorption behavior of the activated carbon, with carbon –oxygen surface structures being by far the most important in influencing surface characteristics (Bansal, et. al 1988, Boehm, 1994). The most common are carboxyl, carbonyl, phenolic hydroxyl, anhydride, ether-type, lactones and lactal. The presence of surface oxygen complexes imparts a polar character to the activated carbon surface, which should affect preferential adsorption of polar organic solutes. The total surface charge of this carbons are for Unactivated cherry seed 1.770 mMolH^+, Activated cherry seed 1.920 mMolH^+ and are comparable with values reported for some commercial grade activated carbons. (Woterella and Marshall, 2000, Toles, et. al 2000) and for rubber seed shell carbon (Okieimen, et. al 2005) rice husk carbon (Ahmedna, et. al 1997) and cassava peel carbon (Ewansiha, et. al 2005).

Moisture content: This is the ratio of weight to the original weight expressed in percentage. The values obtained as presented in table 1.0. for Unactivated cherry seed 9.82, Activated cherry seed 2.65. These values of moisture content reported here are comparable within the range for powdered activated carbons (PACs) in many applications.

Volatile Matter Content: The values obtained for the volatile matter content for this study are for unactivated cherry seed 0.05, Activated cherry seed 47.50. These results meet the permissible volatile content of 0.6-1.4% for blast furnace coke.

Ash Content: Ash content of carbon is the residue that remains when the carbonaceous portion is burned off (James, 1996). The ash consists mainly of minerals such as silica, aluminum, iron, magnesium and calcium. Ash in activated carbon is not desirable and is considered an impurity .The values obtained for the carbons are unactivated cherry seed 0.12%, activated cherry seed 7.5%. These results are an indication of the level of impurity present in them. (Zadok, et al, 1985). The reduction in ash could be attributed to volatilization of some inorganic constituents at higher temperature during activation that could lead to a reduction in ash, and any high value can be attributed to high inorganic component of the carbon .

Table1.1:Results of the physicochemical Characterization of the untreated fishery wastewater.

PARAMETER	UNIT	UNTREATED (RAW)WASTEWATER	FEDERAL MINISTRY OF ENVIRONMENT AND STANDARD (FMES)
PH		6.92±0.00	6.00 – 9.00
TEMP	^oC	29.60±0.00	< 40.00
TURBIDITY	NTU	178.45±_2.00	5.0
ALKALINTY	mg/l	115.90±_2.00	
TSS	mg/L	498.00±_3.00	30.00
TDS	mg/L	302.00±_2.00	500.00
TS	mg/L	800.00±_3.00	

$PO4^{2-}$	mg/L	4.28±0.01	0.005 – 0.1
$SO4^{2-}$	mg/L	7.59±0.01	100.00
NO_3-N	mg/L	13.86±0.01	50.00
NH_4-N	mg/L	79.75±1.00	0.50
DO	mg/L	0.00±0.00	6.80
BOD	mg/L	158.60±2.00	30.40
COD	mg/L	184.00±2.00	80.00
Cd	mg/L	0.17±0.00	<1.00
Cu	mg/L	0.94±0.00	<1.00
Pb	mg/L	0.56±.00	<1.00
Zn	mg/L	1.56±0.00	<1.00
EC	µs/cm	633.00±3.00	

Table 1.2. Results of optimum dosage of powdered Unactivated (UCHC) and Activated (ACHC) carbon from cherry seed (UCHC) with fishery wastewater using COD

Mass of UCHC and ACHC in grams	Volume of Fishery Waste Water in ml	COD in mg/L with Unactivated cherry carbon	% COD Reduction with Unactivated cherry Carbon	COD in mg/L with activated cherry Carbon	%COD Reduction with activated Cherry Carbon
5.0	100	120.00	34.65	114.00	38.04
10.0	100	109.00	41.00	94.50	48.64
15.00	100	100.00	45.65	73.60	60.0
20.00	100	91.00	50.54	88.00	52.17
25.00	100	85.00	53.80	122.00	33.69
30.00	100	94.00	48.91	127.00	30.98
35.00	100	98.00	46.74	136.00	26.08

From Table 1.2, it was observed that 25g of the powdered carbon in 100ml of the wastewater gave 53.80%COD reduction for the unactivated. While that of powdered activated cherry seed carbon was 15g in 100ml of the wastewater which gave 60.00%COD reduction. This then inform the choice of 25g of the carbon for treatment of wastewater with unactivated and 15g for the activated carbon. This is an indication that 25g of the powdered carbon will yield the best treatment with the unactivated and 15g for the activated. A plot of percentage COD reduction against Dose of the carbon for treatment of wastewater from Fishery industry is presented in Figures.1.0 and 1.1

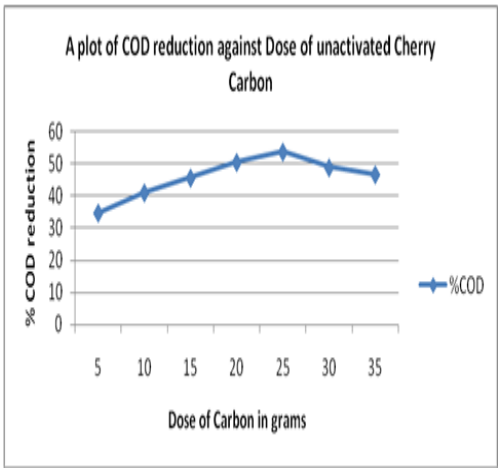

Figure 1.0: COD reduction of unactivated cherry carbon

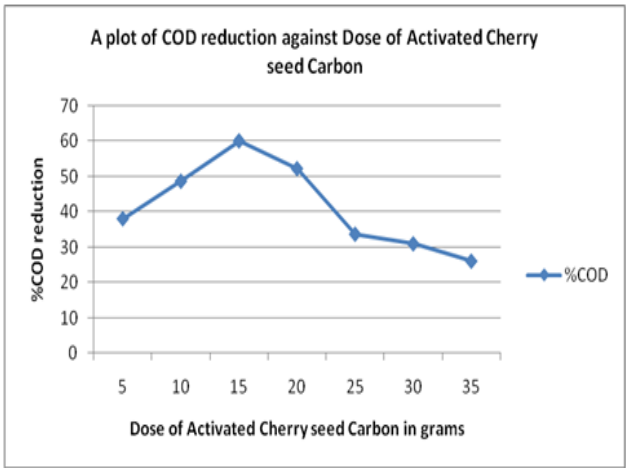

Figure 1.1: COD reduction against dose of activated cherry seed carbon

Table 1.3: Results of the Physicochemical Characterization of Batch Treatment of Fishery wastewater using Unactivated Carbon from Cherry seed (UCHC)

Parameter	Units	untreated W.Water	10mins	30mins	50mins	70mins	90mins	110mins
P^H		6.92±0.00	6.71±0.00	6.81±0.00	7.57±0.00	8.01±0.00	8.03±0.00	8.34±0.00
Temp	C	29.60±0.00	29.90±0.00	29.80±0.00	29.80±0.00	29.90±0.00	30.00±0.00	30.20±0.00
Turbidity	NTU	178.45±2.00	70.52±0.01	56.76±0.00	46.22±0.00	43.43±0.00	25.59±0.00	12.69±0.01
Alkalinity	mg/L	115.90±2.00	113.05±0.02	109.10±0.01	108.35±0.01	106.90±0.01	79.30±0.00	73.20±0.00
TSS	mg/L	498.00±3.00	135.00±0.01	123.00±0.01	119.00±0.01	117.00±0.02	89.00±0.01	78.00±0.01
TDS	,mg/L,	302.00±2.00	218.00±0.03	194.00±0.02	186.00±0.02	158.00±0.01	114.00±0.01	103.00±0.01
TS	mg/L	800.00±3.00	353.00±0.02	317.00±0.02	305.00±0.02	275.00±0.01	203.00±0.01	181.00±0.01
$PO4^{2-}$	mg/L	4.28±0.00	4.24±0.00	4.21±0.00	4.09±0.00	4.04±0.00	3.46±0.00	3.09±0.00
$SO4^{2-}$	mg/L	7.59±0.01	3.64±0.00	3.19±0.00	2.88±0.00	2.70±0.00	2.63±0.00	2.58±0.00

NO_3-N	mg/L,	13.86±0.01	9.70±0.00	9.55±0.00	8.70±0.00	8.34±0.00	7.14±0.00	6.51±0.00
NH_4-N	mg/L	79.75±1.00	35.43±0.01	24.51±0.01	23.51±0.00	21.32±0.00	14.94±0.00	7.22±0.00
DO	mg/L	0.00	3.60±0.00	6.30±0.00	6.40±0.00	7.20±0.00	8.00±0.00	10.20±0.00
BOD	mg/L	158.60±2.00	88.80±0.02	86.20±0.02	68.60±0.01	62.40±0.01	60.40±0.01	56.80±0.00
COD	„mg/L	184.00±2.00	100.00±0.02	92.00±0.01	88.00±0.01	80.00±0.01	74.00±0.00	68.00±0.00
Cd	mg/L	0.17±0.00	0.14±0.00	0.11±0.00	0.11±0.00	0.10±0.00	0.06±0.00	0.04±0.00
Cu	mg/L„	0.94±0.00	0.73±0.00	0.62±0.00	0.60±0.00	0.58±0.00	0.54±0.00	0.41±0.00
Pb	mg/L	0.56±0.00	0.42±0.00	0.35±0.00	0.34±0.00	0.32±0.00	0.30±0.00	0.18±0.00
Zn	mg/l	1.56±0.00	0.88±0.00	0.82±0.00	0.79±0.00	0.72±0.00	0.42±0.00	0.42±0.00
EC	µs/cm	633.00±3.00	574±2.00	432±0.04	412.00±0.02	388±0.02	356.00±0.02	317.00±0.02

Table1.4:Results of the Physicochemical Characterization of Batch Treatment of Fishery wastewater using Activated Carbon Cherry seed (ACHC)

Parameter	Unit	untreated w.water	10 mins	30 Mins	50 Mins	70 mins	90 Mins	110 Mins
P^H		6.92±0.00	7.32±0.00	7.41±0.00	8.25±0.00	8.29±0.00	8.35±0.00	8.43±0.00
TEMP	0^C	29.60±0.00	29.50±0.00	29.60±0.00	29.80±0.00	30.00±0.01	30.30±0.01	30.30±0.00
TURBIDITY	NTU	178.45±2.00	74.35±0.01	65.71±0.01	44.72±0.00	42.14±0.00	41.28±0.00	19.35±0.00
ALKALINITY	mg/L	115.90±2.00	95.55±0.02	83.20±0.02	73.20±0.01	70.00±0.00	67.20±0.00	62.55±0.00
TSS	mg/L	498.00±3.00	129.00±0.02	127.00±0.02	121.00±0.01	117.00±0.01	101.00±0.01	74.00±0.00
TDS	mg/L	302.00±2.00	289.00±0.03	284.00±0.03	244±0.02	228±0.02	225.00±0.02	220.00±0.02
TS	mg/L	800.00±3.00	418±0.04	411.00±0.03	365±0.03	345±0.02	326±0.02	294±0.02
$PO4^{2-}$	mg/L	4.28±0.00	4.21±0.00	4.13±0.00	3.62±0.00	3.29±0.00	3.10±0.00	2.97±0.00
$SO4^{2-}$	mg/L	7.59±0.01	4.30±0.00	3.64±0.00	3.08±0.00	2.58±0.00	2.29±0.00	2.20±0.00
NO_3-N	mg/L	13.86±0.01	10.48±0.01	9.77±0.00	8.32±0.00	7.50±0.00	5.70±0.00	5.22±0.00
NH_4-N	mg/L	79.75±1.00	40.46±0.02	37.78±0.01	35.09±0.01	24.68±0.01	17.13±0.00	15.78±0.00
DO	mg/L	0.00	3.20±0.00	3.60±0.00	4.10±0.00	4.30±0.00	6.40±0.00	8.40±0.00
BOD	mg/L	158.60±2.00	110.40±0.02	98.40±0.01	94.60±0.01	92.40±0.01	88.80±0.01	88.40±0.00
COD	mg/L	184.00±2.00	144.00±0.03	120.00±0.02	110.00±0.01	102.00±0.01	100.00±0.01	100.00±0.01
Cd	mg/L	0.17±0.00	0.12±0.00	0.11±0.00	0.10±0.00	0.09±0.00	0.08±0.00	0.08±0.00
Cu	mg/L	0.94±0.00	0.90±0.00	0.87±0.00	0.84±0.00	0.80±0.00	0.78±0.00	0.77±0.00
Pb	mg/L	0.56±0.00	0.50±0.00	0.48±0.00	0.46±0.00	0.45±0.00	0.43±0.00	0.35±0.00
Zn	mg/L	1.56±0.00	1.46±0.00	1.43±0.00	1.41±0.00	1.38±0.00	1.25±0.00	0.96±0.00
EC	µs/cm	633.00±3.00	614.00±2.00	559.00±2.00	443.00±1.00	426.00±1.00	406.00±0.05	385.00±0.03

Adsorption Isotherms: (Langmuir)

The results of the batch treament of the wastewater using unactivated and activated Cherry seed powdered Carbon obtained at different time intervals was subjected to Adsorption isotherm in order to relate the adsorption concentraion in the bulk and the adsorbed amount at the interface (Eastoe and Dalton, 2000).The isotherm results were analyzed using the Langmuir and Freundlich isotherm .The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface,with no lateral interaction between the sorbed molecules.(Crini, 2006, Hameed, et al 2007). The expression of the Langmuir model is given by Equation

$$q_e = \frac{QobCe}{(1 + bCe)} \quad \text{----------i}$$

Where q_e (mg/g) and Ce (mg/L) are the amount of adsorbed substance per unit mass of sorbent and unadsorbed substance concentration in solution at equilibrium ,respectively.Qo is the maximum amount of adsorbate per unit mass of adsorbent to form a complete monolayer on the surface bound at high Ce and b is a constant related to the affinity of the binding sites (L/mg).

The results of the batch treatment of fishery wastewater using unactivated and activated Cherry seed powdered Carbon obtained at different time intervals were subjected to Langmuir adsorption isotherm. and graphs of Ce/ΔCo against Ce were plotted for each parameter and the values of Langmuir constants Qo (mg/g) and b (L/mg) were obtained from the slope and intercept of the graphs and the correlation coefficient R^2 values are presented in Table 1.5 below.

Table 1.5: Langmuir Isotherm Model constants and correlation coefficients on batch treatment of Fishery wastewater using unactivated and activated cherry seed carbon

Parameters	Qo (mg/g)for unactivated Cherry	b (L/mg)for unactivated Cherry	R^2 for Unactivated Cherry	Qo (mg/g)for activated Cherry	b (L/mg)for activated Cherry	R^2 for activated Cherry
Temperature	==	==	==	==	==	==
Turbidity	0.009	-0.071	0.981	0.011	-0.128	0.983
Alkalinity	0.613	-45.936	0.588	0.106	-0.803	0.937
TSS	0.003	-0.058	0.997	0.003	-0.054	0.994
TDS	0.017	-1.335	0.939	0.248	-53.494	0.956

TS	0.004	-0.539	0.850	0.004	-0.672	0.995
$PO4^{2-}$	==	==	==	==	==	==
$SO4^{2-}$	0.380	-0.473	0.996	0.418	-0.547	0.980
NO3-N	0.446	-2.119	0.950	0.450	-1.948	0.937
NH_4-N	0.025	-0.126	0.969	0.031	-0.269	0.990
DO	==	==	==	==	==	==
BOD	0.022	-0.742	0.994	0.046	-2.877	0.991
COD	0.019	-0.706	0.991	0.054	-4.278	0.968
Cd	===	===	==	===	===	==
Cu	==	==	==	==	==	==
Pb	==	==	==	==	==	==
Zn	==	==	==	==	==	==
EC	0.035	-11.688	0.877	0.113	-45.505	0.738

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L that is given by the following equation (Hall, et. al 1966);

$$R_L = \frac{1}{(1 + bCo)} \quad \text{----------ii}$$

Where Co is the highest initial concentration of adsorbate (mg/L), and b (L/mg) is Langmuir constant .The value of R_L indicates the shape of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$).The R_L values between 0 and 1 indicate favourable adsorption . From table 1.5.0,the correlation coefficient R^2 values for TSS ,$SO4^{2-}$,BOD, and COD for unactivated cherry carbon were 0.99 . While the correlation coefficient R^2 values for TSS, TS, NH4-H, and BOD for the activated cherry seed carbon were 0.99. which indicates a favourable adsorption with Langmuir isotherm for both carbons , while the other parameters had R^2 values between 0.587- 0.981 .

Adsorption Isotherms;(Freundlich)

The results of the batch treament of fishery wastewater obtained at different time intervals for the unactivated and activated cherry seed carbons were equally subjected to Freundlich adsorption Isotherm using $\ln q_e = \ln K_F + (1/n) \ln Ce$, and graph of $\ln q_e$ (log ΔCo) against Log Ce were plotted and the values of K_F, (Freundlich constant),n and1/n were obtained from the slope and intercept respectively, The values are presented in table 1.6.0.below. The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as;

$$q_e = K_F C_e^{1/n} \quad \text{---------- iii}$$

Where K_F and n are Freundlich constants with K_F $(mg/g(L/mg)^{1/n}$ is the adsorption capacity of the adsorbent and n giving an indication of how favourable the adsorption process is ,The magnitude of the exponent ,1/n, gives an indication of the favourability of adsorption.Values of n > 1 represent favourable adsorption condition.(Treybal, 1968, Poots, 1978, Ho, and Mckay,1998.

Table 1.6: Freundlich Isotherm Model constants and correlation coefficients on batch treatment of fishery wastewater using Unactivated and Activated Cherry seed Carbon

Parameters	KF (mg/g(L/mg)1/n for unactivated cherry	n (L/mg) for unactivated cherry	1/n for unactivated cherry	KF (mg/g(L/mg)1/n for activated cherry	n(L/mg) for activated cherry	1/n for activated cherry
Temperature	==	==	=	==	==	=
Turbidity	-0.231	2.490	0.400	-0.307	2.618	0.380
Alkalinity	-5.335	11.660	0.090	-2.317	5.931	0.170
TSS	-0.248	3.091	0.320	-0.217	3.023	0.330
TDS	0.563	1.054	0.950	-6.692	17.639	0.060
TS	-0.490	3.907	0.260	-0.828	4.754	0.210
PO42-	==	==	=	==	==	=
SO42-	-0.691	0.987	1.020	-0.696	0.977	1.020
NO3-N	-1.414	2.026	0.490	-1.313	1.913	0.840
NH4-N	-0.281	2.122	0.480	-0.517	2.439	0.410
DO	=	=	=	==	==	=
BOD	-0.845	3.496	0.290	-1.839	5.438	0.190
COD	-0.841	3.609	0.280	-1.952	5.836	0.170
Cd	==	==	=	=	=	=
Cu	===	==	=	=	=	=
Pb	==	==	=	=	=	=
Zn	==	==	=	=	=	=
EC	-2.532	8.884	0.110	-5.122	15.758	0.060

From Table 1.6 ,it is clear that the batch treatment values for the unactivated and activated cherry seed carbon fits well into the Freundlich isotherm model for both treatments. The values of n were greater than 1 (one)which represent a favourable adsorption .

Adsorption kinetics model:

The results of the batch treatment with unactivated and activated cherry seed carbon were also subjected to Pseudo – first order kinetic model of the Lagergren equation of

$dq_e/d_t = kp\ (q_e - q_t)$ .....(iv)

q_e is the value of the different parameters at t = 0 (untreated wastewater), q_t is the value of the different parameters at different time (Ho, 2006).

This can be rearranged to

$Log(q_e - q_t) = loqq_e - k/2.303t$ ..... (v)

Where qe = Parameters at time t=0 of waste water samples, qt = Parameters of treated samples at different time intervals, K_p = constant, t = time and graphs of (log q_e - q_t) versus time (t) for each parameters was plotted and the values of K_1,q_e and R^2 were obtained from the slopes, intercepts and correlation coefficients of the graphs as shown in Table 1.7.

The batch treatment values of the Unactivated and activated cherry seed carbons were then subjected to Pseudo – first order kinetics model of the Lagergren equation of Log ($q_e - q_t$) = loq qe – kpt/2.30. Graphs of (log q_e - q_t) versus time (t) were plotted as shown in Figures1.2. a, b. and Figures 1.3a,b. The values of K_1(Lagergren rate constant),q_e ,and correlation coefficient R^2 were obtained from the slope ,intercept and correlation coefficient of the graphs and are presented in Table 1.7 below.

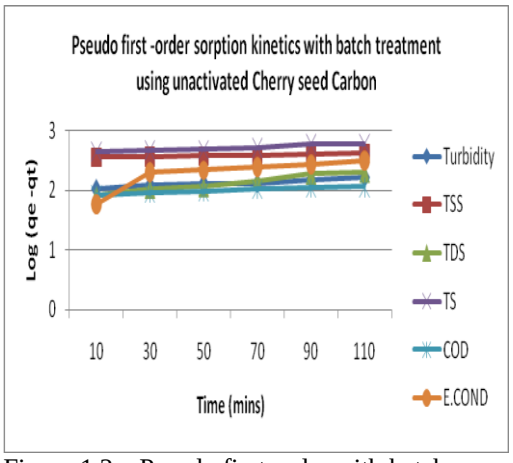

Figure 1.2a: Pseudo first order with batch treatment using activated cherry seed carbon

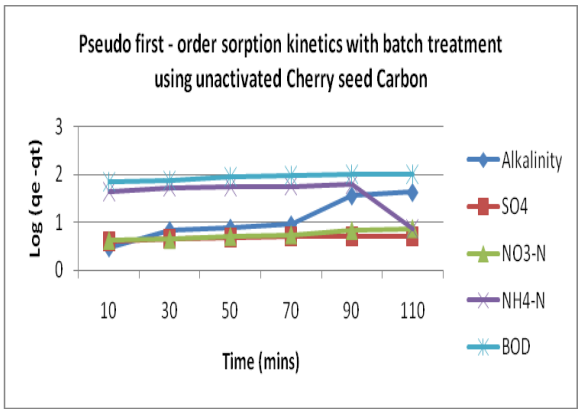

Figure 1.2b: Pseudo first order sorption kinetics with batch treatment using unactivated cherry seed carbon

Adsorption kinetics models for the Activated Cherry seed Carbon:

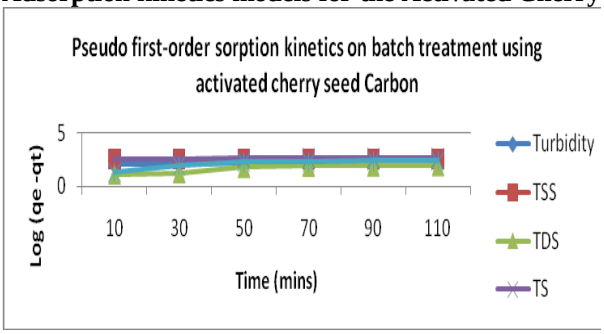

Figure 1.3a: Pseudo first order sorption kintics using activated cherry seed carbon

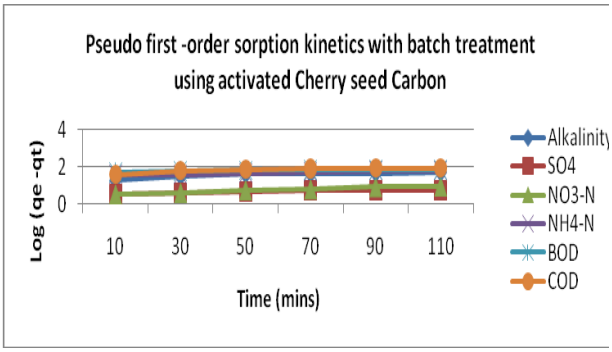

Figure 1.3b: Pseudo first order sorption kintics using unactivated cherry seed carbon

Table 1.7: Pseudo – first –order adsorption kinetics model on batch treatment of fishery wastewater with Unactivated and Activated Cherry seed Carbon

Parameters	K_1 for unactivat	q_e (mg/g)(equilibrium	R^2 for unactivated	K_1 for activated	q_e (mg/g)(equilibrium adsorption capacity for	R^2 for activated

	ed	adsorption capacity for unactivated			activated	
Temperature	==	==	==	==	==	==
Turbidity	546.268	-1101.73	0.952	537.994	-1076.96	0.907
Alkalinity	78.594	-22.654	0.911	221.105	-291.56	0.834
TSS	1536.59	-3914.64	0.921	1453.42	-3701.93	0.809
TDS	251.54	-474.106	0.977	95.581	-96.117	0.819
TS	648.478	-1702.78	0.954	761.768	-1952.34	0.969
PO_4^{2-}	==	==	==	==	==	=
SO_4^{2-}	882.35	-528.24	0.882	440.64	-227.887	0.919
NO_3-N	-368.89	-211.137	0.975	227.77	-111.967	0.979
NH_4-N	-55.92	149.299	0.297	387.167	-598.83	0.957
DO	==	==	==	=	=	=
BOD	505.52	-919.03	0.881	537.93	-906.48	0.799
COD	703.35	-1344.35	0.984	255.567	-409.81	0.719
Cd	==	==	==	==	==	==
Cu	==	==	==	==	==	==
Pb	==	==	==	==	==	==
Zn	==	==	==	==	==	==
EC	117.85	-209.87	0.694	73.839	-93.831	0.745

The results in Table1.7 above showed that the adsorption process for both carbons did not fit into the pseudo – first –order kinetics model since the correlation coefficients R^2 values were less than 0.99.

Pseudo second –order sorption kinetics for activated cherry carbon: The results obtained from the batch treatment process were also subjected to pseudo – second order rate equation (Ho, Mckay, 1998) using the equations below: the driving force ($q_e - q_t$) is proportional to the fraction of the available active sites (Ho, 2006). The pseudo second – order kinetics may be expressed in a linear form as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad \text{.....(vi)}$$

By Plotting graphs values of t/q_t against time (t) for each parameter, the values of K_2 ,q_e and R^2 were determined from the slopes, intercepts and correlation coefficients of the graphs as
shown in Table 1.8.

The values obtained from the batch treatment of Fishery wastewater using Unactivated and Activated Cherry carbons were then subjected to pseudo-second order equation and graphs of t/q_t against time (t) were plotted as shown in Figures 1..4a,b,c,d and Figures 1.5a,b,c. The values of K_2 ,q_e and R^2 were obtained from the slope, intercept and correlation coefficients respectively from the graphs and their values presented in Table1.8 below.

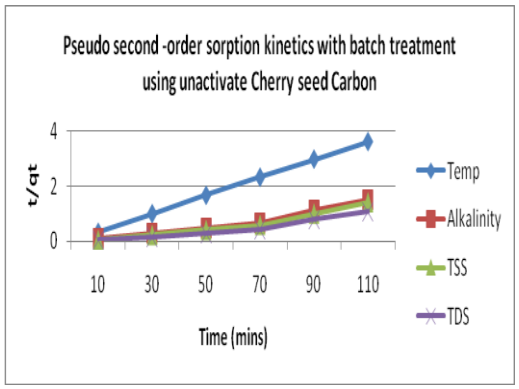

Figure 1.4a: Pseudo second order kinetics using activated cherry seed carbon

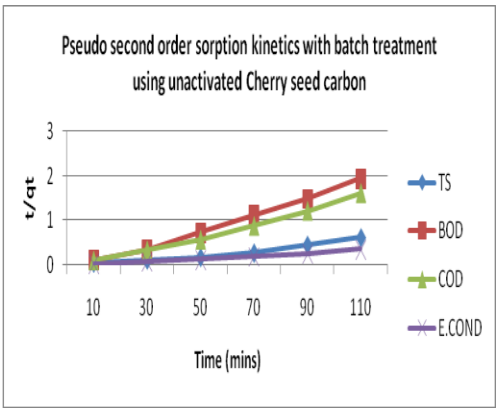

Figure 1.4b:Pseudo second order kinetics using activated cherry seed carbon

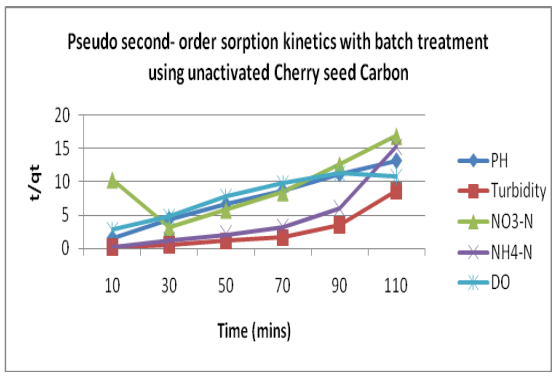

Figure 1.4c: pseudo second order kinetics using activated cherry seed carbon

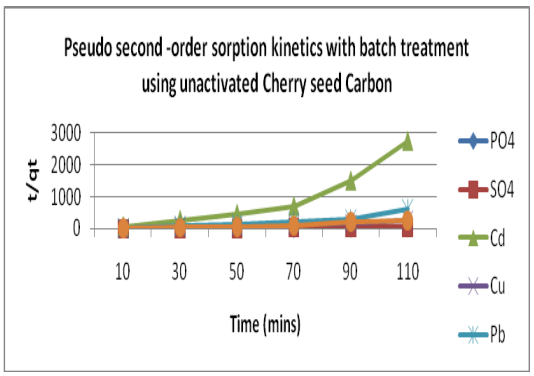

Figure 1.4d: pseudo second order kinetics using activated cherry seed carbon

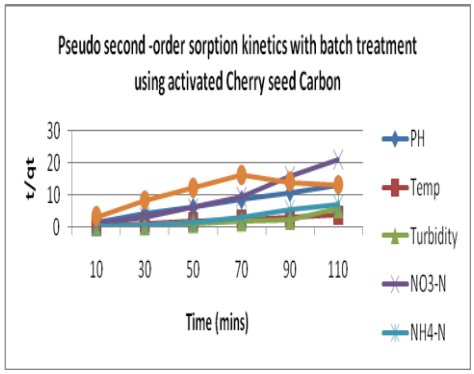

Figure 1.5a: Pseudo second order kinetics using activated cherry seed carbon

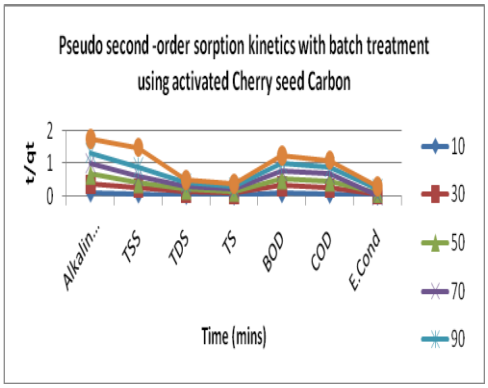

Figure 1.5b: Pseudo second order kinetics using activated cherry seed carbon

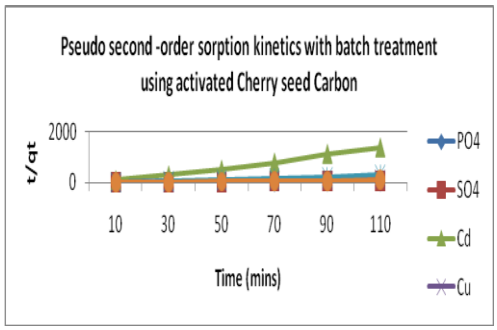

Figure 1.5c: Figure 1.5a: Pseudo second order kinetics using activated cherry seed carbon

Table 1.8: Pseudo – second –order adsorption kinetics model on batch treatment of fishery wastewater using Unactivated and Activated Cherry seed carbon

Parameters	K_2 for unactivated	q_e (mg/g)(equilibrium adsorption capacity for unactivated	R^2 for unactivated	K_2 for activated	q_e (mg/g)(equilibrium adsorption capacity for activated	R^2 for activated
pH	8.614	-5.538	0.997	8.638	-2.985	0.999
Temperature	30.195	-0.391	0.999	30.459	-0.715	0.999
Turbidity	10.162	33.66	0.757	16.493	29.101	0.789
Alkalinity	68.24	13.03	0.958	60.465	7.092	0.994
TSS	72.74	14.535	0.955	70.137	16.631	0.921
TDS	92.32	17.22	0.944	213.609	4.105	0.997
TS	165.34	15.908	0.949	284.382	8.81	0.991
PO_4^{2-}	2.99	9.779	0.974	2.826	7.798	0.993
SO_4^{2-}	2.474	5.439	0.998	2.017	11.862	0.990
NO_3-N	5.291	9.620	0.484	4.736	15.621	0.961
NH_4-N	5.901	32.29	0.761	13.545	20.42	0.936
DO	10.42	-21.81	0.914	6.352	-11.042	0.645
BOD	53.679	8.646	0.993	86.589	3.139	0.999

COD	65.39	8.558	0.990	95.407	4.822	0.999
Cd	0.034	27.33	0.843	0.075	8.478	0.991
Cu	0.397	13.543	0.945	0.752	3.474	0.999
Pb	0.166	21.734	0.863	0.346	9.849	0.967
Zn	0.354	19.58	0.922	0.933	13.215	0.943
EC	305.08	9.66	0.980	277.067	27.213	0.701

The batch treated wastewater values subjected to pseudo sceond order kinetics fit the model and so the Pseudo –second – order model represented the adsorption kinetics better as the values of the correlation coefficient (R^2) in some of the parameters for unactivated cherry seed carbons such as P^H,Temp,SO_4^{2-},BOD,and COD were 0.99 and that of the activated cherry seed carbon such as P^H , Temp, Alkalinity, TDS, TS, PO_4^{2-}, SO_4^{2-},BOD, COD,Cd and Cu were 0.99 and others were within the range of 0.74-0.937 which was close to 0.99 in most of the parameters studied , an indication that the activated cherry seed carbon treated the waste water better than the unactivated carbon . This pseudo second order is based on assumption that the rate limiting step may be chemisorption involving covalent forces through the sharing of electrons between the adsorbent and the adsorbate (Ho and Mckay, 1998). Similar works reported by (Hameed, et. al 2008) on pseudo first and second order revealed low correlation coefficients with first order and a better correlation coefficients with pseudo second order kinetics on the adsorption of methylene blue onto low cost coconut bunch waste.

The results of the batch treatment with unactivated and activated Cherry seed Carbon were also subjected to intraparticle diffusion rate equation (10) as shown below;

$$q_t = K_{id}t^{1/2} + C \qquad \text{……..(vii)}$$

Where K_{id} is the intraparticle diffusion constant. and graphs of each parameters were plotted for q_t against $t^{1/2}$ and values of K_{id} ,C and R^2 were obtained from the slopes, intercepts and correlation coefficients of the graphs as shown in table 1.9. and graphs of q_t against $t^{1/2}$ were plotted as shown in Figures 1.6 a,b. and Figures 1.7 a, b The values of K_{id} (intraparticle diffusion constant), C and correlation coefficient R^2 were obtained from the slope, intercept and correlation coefficient from the graphs and values are presented in Table 1.9 .below.

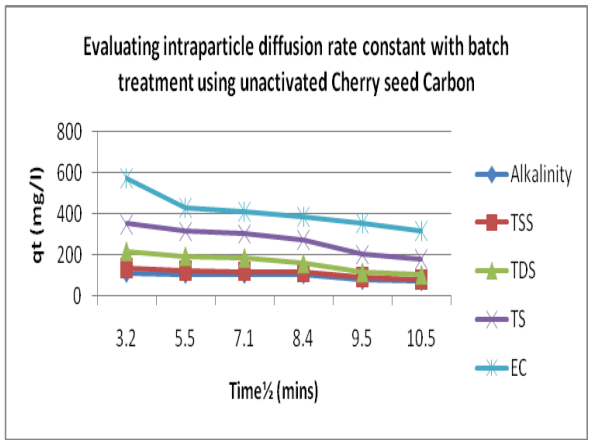

Figure 1.6a: Intraparticle diffusion using unactivated cherry seed carbon

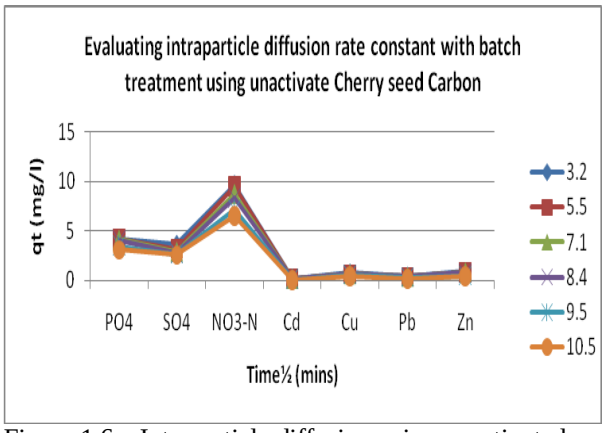

Figure 1.6a: Intraparticle diffusion using unactivated cherry seed carbon

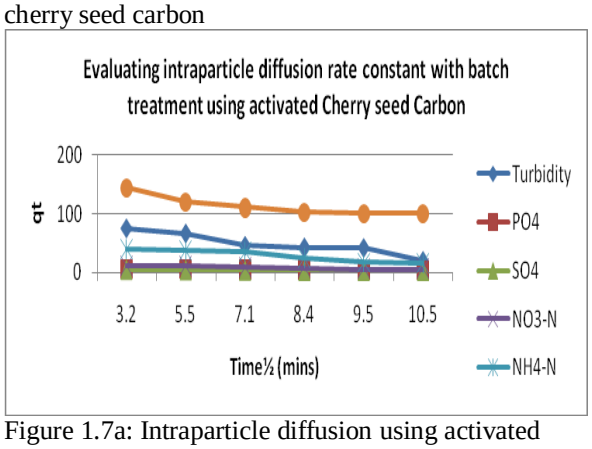

Figure 1.7a: Intraparticle diffusion using activated cherry seed carbon

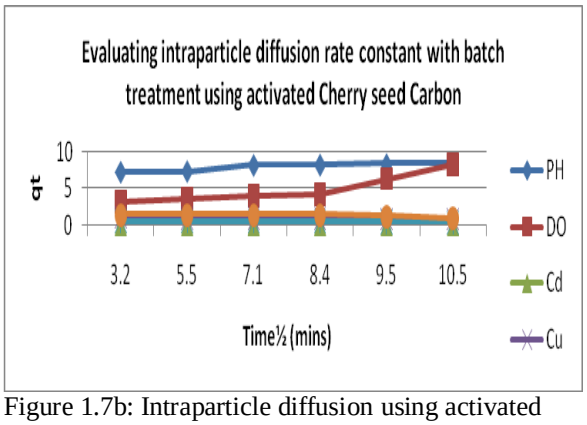

Figure 1.7b: Intraparticle diffusion using activated cherry seed carbon

Table 1.9: Intraparticle diffusion rate constants on batch treatment of fishery wastewater using Unactivated and Activated Cherry seed Carbon

Parameters	K_{id} (intra particle diffusion coefficient for unactivated	C for unactivated	R^2 for unactivated	K_{id} (intra particle diffusion coefficient for activated	C for activated	R^2 for activated
P^H	3.823	-21.608	0.931	4.954	-32.303	0.853
Temperature	12.058	-353.59	0.453	=	=	=
Turbidity	-0.125	92.696	0.941	-0.131	13.663	0.911
Alkalinity	-0.129	20.11	0.694	-0.219	23.927	0.976
TSS	-0.112	19.756	0.831	-0.109	19.550	0.717
TDS	-0.056	16.46	0.911	-0.084	28.184	0.909
TS	-0.037	17.667	0.894	-0.054	26.79	0.940
PO4-	-4.867	26.129	0.720	-4.986	25.083	0.946
SO4-	-6.439	26.276	0.957	-3.237	17.126	0.987
NO3-N	-1.982	23.865	0.889	-1.239	17.069	0.949
NH4-N	-0.272	13.11	0.919	-0.237	14.114	0.892
DO	1.183	-0.852	0.911	1.162	1.555	0.744
BOD	-0.189	20.710	0.926	-0.318	37.766	0.937
COD	-0.223	26.087	0.974	-0.149	24.241	0.912
Cd	-68.514	13.761	0.869	-163.25	23.147	0.977
Cu	-24.054	21.318	0.875	-51.33	49.799	0.981
Pb	-30.666	17.129	0.809	-45.309	27.529	0.776
Zn	-11.769	15.311	0.794	11.409	22.369	0.636
EC	-0.029	19.479	0.931	-0.028	20.743	0.941

From Table1.9,the values of the regression of the plots of q_t versus $t^{1/2}$ for the evaluation of intraparticle diffusion rate constants for the unactivated and activated cherry seed carbons were not linear and so did not pass through the origin, an indication that the intraparticle diffusion rate model was not the sole rate – limiting controlling step and correlation coefficient R^2 values were below 0.99.for both carbons.

IV. Conclusion

This study evaluates the comparative adsorption and kinetic studies of the treatment of wastewater using a cost effective and efficient carbons developed from Cherry seed shells. In this study, both activated and the unactivated carbons were prepared from Cherry seed and characterized, used as adsorbent in the treatment of wastewater from fishery industry through batch column treatment process (BCT). The data obtained revealed that both powdered activated and unactivated carbon has the ability of adsorbing organic and inorganic materials from aqueous medium .The parameters studied fits well into the Langmuir and Freundlich isotherm models for both carbons .The adsorption kinetics studies revealed that most of the parameters did not fit well into the Pseudo –first –order kinetics sorption and the Intraparticle diffusion rate constant models for both carbons. The adsorption kinetics can best be described by pseudo –second –order model equation since some of the parameters treated with the unactivated cherry carbon fits in and more of the parameters treated with the activated cherry carbon fits well into the pseudo-second –order kinetics sorption with the correlation coefficient values R^2 equal to 0.99.

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