

EVALUATION OF THE ADSORPTION POTENTIAL OF RUBBER (*Hevea brasiliensis*) SEED PERICARP-ACTIVATED CARBON IN ABATTOIR WASTEWATER TREATMENT AND IN THE REMOVAL OF IRON (III) IONS FROM AQUEOUS SOLUTION

S.E. Agarry^a, C.N. Owabor^b

^aBiochemical Engineering and Biotechnology Laboratory, Department of Chemical Engineering, Ladoke Akintola University of Technology, Ogbomoso, Nigeria. *Email: sam_agarry@yahoo.com* ^bDepartment of Chemical Engineering, University of Benin, Benin-City, Nigeria. *Email: owabor4you@yahoo.com*

Abstract

The objective of this study was to produce activated carbon from rubber seed pericarp and to evaluate its performance with commercial activated carbon in the treatment of abattoir wastewater as well as its potential in the adsorption of iron (III) ions from aqueous solution. The rubber seed pericarp was carbonized at 400°C and activated with zinc chloride at 800°C to produce Rubber Seed Pericarp Activated Carbon (RSPAC). The results indicated that the treatment efficiency of RSPAC was about 40 - 99% as that of the commercially supplied activated carbon. From the iron (III) batch adsorption studies, the experimental batch equilibrium data was correlated by Freundlich, Langmuir and Temkin isotherms. The Langmuir isotherm model provided the best correlation of the experimental data while the Lagergren pseudo-first order kinetic equations could describe the adsorption kinetics very well. Thus, it was implied that RSPAC may be suitable as adsorbent material for wastewater treatment.

Keywords: abattoir waste water, activated carbon, adsorption isotherms, iron (III) chloride, lagergren equations, rubber seed pericarp

1. Introduction

The presence of organic chemicals and heavy metal ions in aquatic systems as a result of the discharge of domestic and industrial wastewaters poses a major threat to the environment, due to their acute toxicity to many life forms [1]. The continuous drive to increase meat production for the protein needs of the ever increasing world population has led to increase in the rearing of cows, goats, sheeps and pigs as well as increase in the number of small and large scale slaughter (abattoir) houses and meat processing industries. In many countries, pollution arises from activities in meat production as a result of failure in adhering to Good Manufacturing Practices (GMP) and Good Hygiene Practices (GHP) [2]. The abattoir uses large quantities of water and generates equally large quantities of biodegradable organic wastewater with medium to high strength, containing large amounts of fats, oil, grease, blood, urine, manure, hair, grit, meat tissue, suspended particles of semi-digested and undigested food within the stomach and intestine of slaughtered animal; thereby contributing to the pollutant load of water bodies [3 5]. Abattoir wastewaters generated in small abattoirs in Nigeria are usually discharged into the nearby drains which carry the city sewage without any adequate treatment causing a serious and deleterious threat to human health and also to the surface water quality. In addition, iron ions are attracting wide attention of researchers as one of the heavy metals found in ground and industrial waters and become toxic at high level which causes environmental and human health problems [1]. However, the ever increasing demand for water has caused considerable attention to be focused towards recovery and re-use of waste waters [6] and contaminated water. Generally, there are various technological methods that exist for removing organic chemicals and heavy metal ions from water and wastewater including supercritical fluid extraction [7], bioremediation [8], catalytic wet oxidation [9]

WASTEWATER TREATMENT ADSORPTION POTENTIAL OF RUBBER SEED PERICARP-ACTIVATED CARBON 347

and adsorption [10].

Adsorption on activated carbon is one of the most efficient techniques used in water treatment process for the removal of organics and micro pollutants from wastes and drinking waters [11]. Adsorption processes have long been used in the removal of colour, odour, organic and inorganic pollutants [12 - 13]. These processes are usually based on the use of activated carbon [11]. Activated carbon has been reported to have high and fast adsorption capacities [14] due to its well developed porous structure, high surface area and high degree of surface reactivity [15]. However, because of high cost of commercial activated carbon, its use in the field is sometimes restricted on economical considerations especially in developing countries like Nigeria. As such, attempts have been made by different researchers to develop alternative adsorbents preferably of low cost for the removal of pollutants. Both industrial wastes as well as natural agricultural byeproducts such as fly ash, corncob wastes, spent bleaching earth, apricot stone shells, rubber seed coat, waste tyre rubber, rice husk, groundnut husk, fertilizer waste slurry, coconut husk, peanut null, moringa oleifera seed husk and saw dust [16 - 20] have been utilized for this purpose. Reports from literature have shown that the composition of agricultural bye-products has a strong influence on the final porous and chemical features of the solid products obtained from pyrolysis and carbon activation [21 - 22]. Cabal et al. [22] have reported that high contents of cellulose in agricultural bye-products yield predominantly microporous materials, whereas high content of lignin favour the development of a macroporous structure when converted to carbonaceous adsorbents. It has also been reported from earlier works that adsorbents obtained from agricultural by-products need further modifications as to increase the active binding surfaces and to make them readily available for sorption [23 - 24]. It is stated that these modifications involves pretreatment with chemicals like HCl, H₂SO₄, ZnCl₂, H₃PO₄, alkaline hydroxides and physical pretreatment using steam or carbon dioxide to remove surface impurities on the adsorbents and expose the available binding sites for pollutant adsorption [23 - 25]. A survey of literature reveals that although a large number of alternative adsorbents have been studied to replace activated carbons, the results have been very promising [22, 26– 28]. Mohammed, et al. [26] studied the adsorption of phenol from aqueous solution using local granular activated carbon produced from palm date pits and compared it to a commercial activated carbon sample (Filtrasorb-400). They observed that the locally prepared activated carbon from palm date pits was more efficient in phenol adsorption than the commercial sample. Also, Amuda and Ibrahim [27] compared the adsorption efficiency of coconut shell-based granular activated carbon with the adsorption efficiency of commercial carbon, (Calgon carbon F-300), with respect to organic matter from a beverage industrial wastewater. Their studies revealed that the acid activated coconut shell carbon had higher adsorption for organic matter than calgon carbon (F-300) at all carbon dosages used.

However, some of the adsorbents studied have poor capacity as compared to activated carbons and are also not versatile in adsorbing different types of pollutants. Furthermore, some of the adsorbents developed are not really low cost materials to permit widespread use. Therefore, efforts are still needed to produce low cost adsorbents that have high adsorption capacity. More also, the treatment of abattoir wastewater using biological methods such as anaerobic digestion has been mostly reported [29, 30]. However, there is a dearth of information on the physical treatment of abattoir wastewater using the adsorption technology. Thus, this study was undertaken with the aim to study the adsorption behaviour of prepared activated carbon from the pericarp of rubber fruit which has not been reported for the treatment of abattoir waste water and the removal of iron (III) ions from aqueous solutions.

2. Materials and Method

2.1. Materials

Abattoir wastewaters were obtained from two different sources; Atenda Slaughter House located along Atenda Road in Ogbomoso, Oyo State, Nigeria and Ewah Slaughter House along Ewah Road, Off Ikpoba Slope, Benin-City, Edo State, Nigeria. Pericarp of rubber fruit obtained from a rubber factory in Sapele, Nigeria. Alls reagents used in the present study were of analytical grade. These include potassium iodide and sodium thiosulphate used for iodine number determination;

2.2. Method

2.2.1. Preparation of activated carbonaceous adsorbent

The starting raw material, pericarp of rubber fruit (agricultural by-product) was sun dried and cut into pieces. It was then placed in a stainless steel container with a cover and put in a furnace. The sample was heated at 400°C for a period of 3h. After the pyrolysis, the pyrolysed sample (residual char) was allowed to cool and washed with deionized water to remove any left impurities. The washed residual char was dried in an oven at 110°C for 1h. The next step was the chemical activation. This was done by mixing 100g of the residual charcoal with 200ml of zinc chloride and left for 48h. After decantation, the sample was pyrolysed at 800°C for 3h in a furnace. The obtained activated carbon was allowed to cool and then washed with HCl and deionized water. It was then dried in an oven at 110°C for 3h.

2.2.2. Particle sizing of adsorbent

The activated carbon was grounded into powder form and passed through different standard sieves and fractions corresponding to 100 - 150 mesh (i.e. 0.099- 0.149 mm) and 200 - 250 mesh (0.058 - 0.074 mm) were collected and stored in a dessicator.

2.2.3. Characterization of the prepared adsorbents

The carbonaceous adsorbents were characterized for iodine number in accordance with ASTM [31] and surface area determined by nitrogen gas adsorption method with a surface area measuring instrument, Gemini 2375 (Micrometrics). The iodine number gives an indication of the adsorption capacity of activated carbon in microspores (that is, an indication of porosity) [16]. For the determination of iodine number, 0.1g of the sample was taken into a 250 ml conical flask. About 10 ml 0.05 M iodine solution in aqueous potassium iodide was added into the flask. After 1 h, the solid mass was separated by centrifuging the mixture and the residual iodine in solution was titrated using 0.1 M sodium thiosulphate solution. The iodine number was calculated as mg of iodine adsorbed by one gram of activated carbon. The samples of carbonaceous adsorbent were tested for pH by stirring with deionized water for 2 h and left for 24 h after which the pH of the water was taken.

2.2.4. Characterization of the abattoir wastewater

The physical and chemical parameters of the wastewater were analyzed and determined in triplicates for pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total solids (TS), total suspended solids (TSS), total dissolved solids (TDS), iron, sulphate and nitrate using standard methods [32].

2.2.5. Adsorption efficiency of prepared adsorbents

To assess the effect of the Rubber Seed Pericarp Activated Carbon (RSPAC) on the physical and chemical parameters of the wastewater (that is treatment), 3g of RSPAC was added to 20ml of the wastewater in a conical flask. The conical flask was corked and thoroughly agitated on a magnetic stirrer for 4h. This procedure was repeated for the commercially supplied activated carbon (CSAC).

2.2.6. Batch adsorption studies

The RSPAC was used to study the adsorption of iron (III) ions. The adsorption equilibrium study of iron ions was carried out in a 250 ml-corked flask by adding 3g of RSPAC (with particle size of 0.099 -0.149 mm) to 20ml of iron (III) chloride (FeCl₃) solution. The concentrations of iron (III) in the FeCl₃ solution were varied in the range of 50 to 200mg/l. All the experiments were done at room temperature. After thorough agitation or shaking for 4h on a magnetic stirrer, contents were filtered and the filtrate was analyzed for iron (III) ions using an automated spectroanalytical instrument that employs the inductively coupled plasma atomic emission spectroscopy concept. The same procedure was repeated for RSPAC with particle size of 0.058 - 0.074 mm and an adsorbent dosage that varied from 1 to 10g, respectively. The amount of iron (III) adsorbed at equilibrium, (mg/g) was calculated according to Equation (1) [33]:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

Where C_0 and C_e (mg/l) are the initial and final (equilibrium) concentrations of iron (III) in waste water. V(ml) is the volume of the waste water and W (g) is the mass of dry adsorbent used.

2.2.7. Batch kinetic studies

The batch kinetic experiments were basically identical to those of adsorption equilibrium methods. The aqueous samples were taken at time intervals of 10 min and the concentrations of iron (III) ions were similarly measured. All the kinetic experiments were carried out at 30°C at an initial concentration of 50, 75, 100, 125, 150, 175 and 200 mg/l. The amount of iron (III) adsorbed at time t, q_t was calculated according to Equation (2) [34]:

$$q_t = \frac{(C_o - C_t)V}{W} \tag{2}$$

Where C_t is the concentration of iron (III) in waste water at time t. The percentage of iron (III) ions removal was calculated using Equation (3) [35]:

Removal (%) =
$$\frac{C_o - C_t}{C_o} \times 100$$
 (3)

3. Results and Discussion

3.1. Characterization of the rubber seed pericarp activated carbon

The characterization of RSPAC shows that it has an iodine number of $1275m^2/g$ and a surface area of $1495m^2/g$. The value of iodine number for RSPAC revealed that the adsorbent is significantly porous and this porosity imparts a higher surface area to the adsorbents which was confirmed by the high surface area value obtained. The interaction of RSPAC with deionized water showed that pH of the water was lowered, which indicates that the prepared carbonaceous adsorbent comes under 'L' type carbon according to Steenberg Mattson classification (No.7). Table 1: Physical and chemical characteristics of abattoir waste water from Benin and Ogbomoso source in comparison with FEPA and W.H.O standards. (TSS = Total Suspended Solids, TDS = Total Dissolved Solids, BOD = Biological Oxygen Demand, COD = Chemical Oxygen Demand. N/A = Not Available)

Parameters	Benin	Ogbomoso	FEPA	W.H.O
	Source	Source		
pН	7.7	8.5	6-7	N/A
Iron (mg/l)	50	125	20	0.3
Sulphate	615	1054	500	250
(mg/l)				
Nitrate	50.3	120.5	20	50
(mg/l)				
TSS (mg/l)	2991	3900	30	N/A
TDS (mg/l)	2480	3496	2000	1000
BOD (mg/l)	57	152	30	N/A
COD (mg/l)	615	1054	N/A	N/A

3.2. Characterization of the abattoir wastewater

Table 1 show the characteristic results of the pretreated abattoir wastewater in comparison to Federal Environmental Protection Agency (FEPA) [36] and World Health Organization (W.H.O) [37] permissible limit in surface and ground water. The strength of an effluent is quantified by its Biological Oxygen Demand (BOD) and it's Chemical Oxygen Demand (COD) [3]. The results revealed that the physicochemical parameters of the abattoir waste water from Benin and Ogbomoso source have higher values than the permissible limit for surface waters as given by FEPA [36] and W.H.O [37]. However, the physicochemical parameters of abattoir waste waters from Ogbomoso source are greater than that from Benin source. The high level of these parameters in water bodies makes them toxic to both aquatic and human life.

3.3. Effect of adsorbent on the physicochemical parameters of abattoir wastewater

Table 2 shows the effect of RSPAC and CSAC on the physicochemical parameters of the abattoir wastewater and the adsorption efficiency of RSPAC in comparison with CSAC (post-treated waste water). It was observed that both the RSPAC and CSAC were able to reduce the physicochemical parameters to or below the permissible level required for surface waters. The results also indicate that RSPAC is 40 - 99% as efficient as CSAC. Therefore, RSPAC was used for subsequent studies.

3.4. Effect of contact time and concentration

To determine equilibrium time for the maximum uptake of iron (III) ions, their adsorption at fixed concentration on RSPAC was studied as a function of time and the results are shown in Figure 1. It was observed that the rate of iron (III) uptake was rapid in the beginning and that half of the ultimate adsorption was completed in less than an hour. Also, it was observed that the time required for equilibrium adsorption is 1h. The effect of initial iron (III) concentrations on equilibrium time at different concentrations was also investigated and the result shown in Figure 1. The plots showed that time of equilibrium as well as time required to achieve a definite fraction of equilibrium adsorption was independent of initial concentration. This observation was also made by Ajay et al. [19] when they studied the kinetics of phenol adsorption on powdered activated carbon. The adsorption capacity at equilibrium increased with increase in initial iron (III) ions concentration (Figure 1). This is due to increasing concentration gradient which acts as increasing driving force to overcome the resistances to mass transfer of iron (III) ions between the aqueous phase and the solid phase [38]. Similar results were obtained in the adsorption of lead, nickel and cadmium ions onto tea waste [39] and the adsorption of lead ions onto calcareous soil [40]. However, the percentage removal of iron (III) ions decreased with the increment of the initial concentration. This observation is due to the fact that all adsorbent have a limited number of active sites and at a certain concentration the active sites become saturated [41].

3.5. Effect of particle size

Figure 2 shows the effect of particle size on the adsorption of iron (III) ions from aqueous solutions. It was found that the adsorption capacity increased to some extent with a decrease in particle size of the adsorbent. This could be due to substantial increase in surface area and larger pore volume. The access to all pores is facilitated as particle size becomes smaller. Similar results were obtained by Rao et al.[42], and Ajay et al [19]. Also, on each isotherm the amount of iron (III) ions adsorbed increased with feed concentration and leveled off at higher concentration.

3.6. Effect of adsorbent dosage

The effect of adsorbent dosage on iron (III) ions adsorption was investigated as shown in Figure 3. It could be seen that the percent removal of iron (III) ions increases with the increase in the amount of adsorbent. This kind of a trend is mostly attributed to an increase in the adsorptive surface area and the availability of more active binding sites on the surface of the adsorbent [40, 42]. Similar results were obtained by Ananadurai et al. [6] and Annadurai and Kritshnan [44] owing to increase in the number of sites.

3.7. Adsorption isotherms

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in

Table 2: Characteristics of Abattoir Wastewater before and after Treatment with RSPAC and CSAC. (% RE = Percent reduction (or removal))

		BENIN S	SOURCE		OGBOMOSO SOURCE				
Parameters	CSAC	% RE	RSPAC	% RE	CSAC	% RE	RSPAC	% RE	
pH	6.5	16	6.7	13	6.5	24	6.7	21	
Iron	6.0	88	6.3	87.4	13.2	89	13.6	89	
Sulphate	214	65	215	65	366.8	65	368	65	
Nitrate	8.5	83	8.9	82	19.8	84	20	83	
TSS	20	99	18.8	99	25.8	99	24.8	99	
TDS	1380	44	1403	43	1945	44	1969	44	
BOD	15	68	17.5	69	48	68	47.2	69	
COD	32	95	33.5	95	80	92	81.7	92	



Figure 1: Effect of Contact Time and Initial Iron (III) ions Concentration on the Adsorption of Iron (III) ion onto Rubber Seed Pericarp Activated Carbon.



Figure 2: Effect of Adsorbent Particle Size on the Adsorption of Iron (III) onto Rubber Seed Pericarp Activated Carbon.



Figure 3: Effect of Adsorbent Dosage on the Adsorption of Iron (III) ions onto Rubber Seed Pericarp Activated Carbon.

the liquid phase and that on the adsorbents surface at a given condition. A number of isotherms have been developed to describe equilibrium relationships. In the present study, Langmuir, Freundlich and Temkin models were used to describe the equilibrium data. The results are shown in Table 3 and the modeled isotherms are plotted in Figure 4.

3.7.1. Langmuir isotherm

Langmuir isotherm model [45] is as given in Equation (4):

$$q_e = \frac{KaC_e}{1+aC_e} \tag{4}$$

Where q_e is the amount adsorbed at equilibrium concentration, K is the Langmuir constant. K is a measure of the amount of ions adsorbed when saturation is attained (i.e. related to the maximum monolayer capacity), "a" is the Langmuir constant related to the energy of adsorption, and C_e is the equilibrium liquid phase solute concentration. Langmuir equation is valid for monolayer sorption unto a surface with a finite number of identical sites which are homogeneously distributed over the sorbent surface [25]. The basic assumption of Langmuir model is that sorption takes place at specific sites within the adsorbent. Theoretically, therefore, a saturation value is reached beyond which no further sorption can take place. A plot of $1/q_e$ versus $1/C_e$ resulted in a linear graphical relation indicating the application of the above model as shown in Figure 4.

The values of K and a have been evaluated from the intercept and slope of these plots representing the different particles sizes, and are given in Table 3. It can be observed that the monolayer capacity (K) of the adsorbent for iron (III) ions is comparable to the maximum adsorption obtained. It can be explained apparently that when a > 0, sorption system is favorable (Chen et al., 2008). In this study, a was found to be 0.0033 1/mg and the maximum monolayer adsorption capacity (K) was obtained to be 25 mg/g for iron (III) ions adsorption onto RSPAC with particle size of 0.099-0.149 mm, while a and K are 0.0063l/mg and 50 mg/g, respectively, for the adsorption of iron (III) onto RSPAC of 0.058-0.074 mm particle size. Therefore, the values of K and a show that as the particles size decreases, the removal of iron (III) ions increases which is due to larger surface area associated with small particles. For larger particles the diffusion resistance to mass transport is higher and most of the internal surface of the particle may not be utilized and consequently the amount of iron (III) ions adsorbed is small [46]. From previous studies of iron (III) adsorption onto other adsorbents in the literature, Sirichote et al. [47] obtained 12.35 mg/g, 26.65 mg/g and 42.9 mg/g as the maximum monolayer adsorption capacity of activated carbon derived from coconut shell, pericarp of rubber fruit and bagasse, respectively. Ngah et al. [48] and Karthikeyon and Ilango [49] have correspondingly reported a value of 90.09 mg/g and 1.18 mg/g as the maximum adsorption capacity of chitosan beads and activated carbon derived from Recinius Communis Linn, respectively. While Abassi et al. [51] reported a negative value of -16.35 mg/g as the maximum adsorption capacity of raphia palm fruit endocarp. Moreover, it is also clear from the shape of the adsorption isotherm that it belongs to the L2 category of isotherm, which indicates



Figure 4: Langmuir isotherm fitted to the batch adsorption data obtained for iron (III) ions adsorption onto rubber seed pericarp activated carbon.

the normal or Langmuir type of adsorption [50]. L2 shape of isotherm observed in the present case clearly implies that iron (III) ions must be strongly attached to pericarp of rubber seed generated activated carbon. The essential characteristics of Langmuir isotherms can be described by a separation factor [15], which is defined by Equation (5):

$$R_L = \frac{1}{(1+aC_o)} \tag{5}$$

Where C_o is the initial iron (III) ions concentration. The separation factor (R_L) indicates the isotherm shape as follows: $R_L > 1$ unfavourable, $R_L = 1$ linear, $0 < R_L < 1$ favourable and $R_L = 0$ irreversible. For this experiment, the values of R_L less than one are given in Table 4 indicating favourable adsorption.

3.7.2. Freundlich isotherm

The Freundlich isotherm model [52] is given in Equation (6):

$$q_e = K_f C_e^{1/n} \tag{6}$$

Where K_f and n are Freundlich constants. K_f is roughly an indicator of the adsorption capacity (mg/g) and n is the adsorption intensity. The Freundlich isotherm is used for non-ideal adsorption on heterogeneous surface energy systems [6]. It suggests that binding sites are not equivalent and/or independent. McKay et al. [53] and Annadurai et al. [54] have stated that the magnitude of the exponent 1/n gives an indication of the favourability and capacity of the adsorbent/adsorbate system. Values n > 1 represent favourable adsorption conditions according to Treybal [55]. In most cases, the exponent between 1 < n < 10 shows beneficial adsorption. K_f and 1/n were determined from the linear plot of $\log q_e$ vs $\log C_e$ as shown in Figure 5.

The evaluated constants are given in Table 3. In this study, K_f and 1/n were found to be 0.431 mg/g and 0.833, respectively for iron (III) adsorption onto RSPAC with particle size of 0.058-0.074 mm while K_f and 1/n were 0.084 mg/g and 0.973, respectively, for the adsorption of iron (III) onto RSPAC of particle size, 0.099-0.149 mm. This indicates that (K_f) decreased with increase in adsorbent particle size. Thus, n value is 1.03 and 1.20 for adsorbent particle size of 0.099-0.149 and 0.058-0.074 mm, respectively. From other studies in the literature, the value of K_f : nobtained for the adsorption of iron (III) ions onto other adsorbents are: 55.3:3.32 for chitosan beads [48], 3.71:1.35 for activated carbon derived from Recinius communis Linn [49] and 3.98:0.690 for raphia palm fruit endocarp [51].

3.7.3. Temkin isotherm

Temkin isotherm model [56] was also used to fit the experimental data. Unlike the Langmuir and Freundlich equation, the Temkin isotherm takes into account the interactions between adsorbents and organic chemicals to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage [57]. Temkin model is given in Equation (7):

$$q_e = \frac{RT}{b_T} \ln(AC_e) \tag{7}$$



Figure 5: Freundlich isotherm fitted to the batch adsorption data obtained for iron (III) ions adsorption onto rubber seed pericarp activated carbon.

The linear form of the Temkin isotherm is represented as:

$$q_e = B\ln A + B\ln C_e \tag{8}$$

Where C_e is concentration of the sorbate at equilibrium (mg/l), q_e is the amount of sorbate adsorbed at equilibrium (mg/g), $RT/b_T = B$ where T is the temperature (K), and R is the ideal gas constant $(8.314 \times 10^{-3} \text{ KJ mol}^{-1} \text{ K}^{-1})$ and A and b_T are constants. A linear plot of q_e vs $\ln C_e$ (Figure 6) enables the determination of constants A and B. The constant B is related to the heat of adsorption and A is the equilibrium binding constant (l/min) corresponding to the maximum binding energy. The values of A, B and b_T are given in Table 3. The lower values of b_T (i 8 KJ/mol) indicate that the interaction between iron (III) ions and RSPAC was weak. Hence, the adsorption process of iron (III) onto RSPAC can be expressed as physisorptions as indicated by the value of b_T (= 1.66 kJ/mol) for iron (III) adsorption onto RSPAC with 0.099-0.149 mm particle size, and b_T (= 1.08 kJ/mol) for the adsorption of iron (III) onto RSPAC of particle size, 0.058-0.074 mm).

Generally, all the tested isotherm models fitted well to the equilibrium adsorption experimental data with high correlation coefficient, however, the Langmuir isotherm model provided the best fit with a higher correlation coefficient ($R^2 = 0.993$) to describe the adsorption process. A similar observation has been reported for the adsorption of iron (III) ions onto activated carbon derived from coconut shell [58], activated carbon obtained from Recinius Communis Linn [49] and chitosan beads [48].

Table 4: Langmuir Isotherm with Separation Factor (R_L) at Different Particle Sizes.

Initial Iron (III)	Particle Size (mm)				
Concentration $(mg/1)$	0.099-0.149	0.058-0.074			
50	0.8584	0.7605			
75	0.8013	0.6791			
100	0.7519	0.6135			
125	0.7080	0.5594			
150	0.6689	0.5141			
175	0.6337	0.4756			
200	0.6024	0.4425			

3.7.4. Kinetics of adsorption

The kinetics of adsorption is important from the point of view that it controls the process efficiency. Various adsorption kinetic models such as Lagergren pseudo first-order, pseudo second-order and intra particle diffusion have been used by different workers [50, 59] to elucidate the mechanism by which pollutants are adsorbed. Different adsorption systems conform to different adsorption kinetic models.

3.7.5. Lagergren pseudo first-order kinetic model

The Lagergren rate equation [60] is the most widely used [59] for the adsorption of a solute from a liquid solution. Thus for the first order equation is given In Equation (9):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$
 (9)

Where q_e and q_t are amounts of iron (III) ions adsorbed (mg/g) at equilibrium and at time t respec-



Figure 6: Temkin isotherm fitted to the batch adsorption data obtained for iron (III) ions adsorption onto rubber seed pericarp activated carbon.

Ta	b	le	3:	Langmuir,	Freundlich	and	Temkin	$\operatorname{constants}$	at	$\operatorname{different}$	particle	sizes
----	---	----	----	-----------	------------	-----	--------	----------------------------	---------------------	----------------------------	----------	-------

Particle size	Langmuir			Freundlich			Temkin			
(mm)	K (mg/g)	$C (mg/g) = a (l/mg) = R^2$		$K_f (mg/g)$	1/n	R^2	A	B	b_T	R^2
0.058 - 0.074	50	0.0063	0.975	0.431	0.833	0.935	0.383	2.34	1.08	0.956
0.099 - 0.149	25	0.0033	0.993	0.084	0.973	0.988	0.152	1.52	1.66	0.911

tively, and k_1 (the first order rate constant) was applied to the present studies. As such, the values of $\log(q_e - q_t)$ were calculated from the kinetic data of Figure 1 and plotted against time as shown in Figure 7. A linear relationship observed in the semi-log plot is indicating the applicability of the above equation and the first order of the process. The first order rate constants calculated from the plots are given in Table 5.

3.7.6. Pseudo second-order kinetic model

The pseudo-second- order kinetic model which is based on the assumption that chemisorption is the rate-determining step and can be expressed as in Equation (10) [35]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(10)

Where k_2 is the rate constant of second order adsorption (g/mg/min). Values of k_2 and q_e were calculated from the plots of t/q_t vs. t as shown in Figure 8 for two different initial concentrations.

The respective constant values are given in Table 5.

3.7.7. Intra particle diffusion model

The intra particle diffusion kinetic model [61] can be written as presented in Equation (11):

$$q_t = K_p t^{1/2} + C (11)$$

Where K_p is the intra particle diffusion rate constant $(mg/g min^-)$ and C is the intercept.

The intercept of the plot reflects the boundary layer effect. Larger the intercept, greater is the contribution of the surface sorption in the rate controlling step. Intra particle diffusion is the sole rate-limiting step if the regression of q_t vs $t^{1/2}$ is linear and passes through the origin [61]. In fact, the linear plots at each concentration (Figure 9) did not pass through the origin. This deviation from the origin is due to difference in the rate of mass transfer in the initial and final stages of the adsorption. This indicated the existence of some boundary layer effect and further showed that intra particle diffusion was not the only rate limiting step. The calculated diffusion coefficient values are listed in Table 5. The K_p value increased with increase in initial iron (III) concentration.

Generally, all the tested adsorption kinetic models fitted well to the adsorption kinetic data with high correlation coefficient at different initial iron (III) concentrations; however, the Lagergren first-order gave the



Figure 7: Lagergren first-order kinetic model fitted to the batch adsorption data obtained for iron (III) adsorption onto rubber seed pericarp activated carbon.



Figure 8: Pseudo second-order kinetic model fitted to the batch adsorption data obtained for iron (III) adsorption onto rubber seed pericarp activated carbon.



Figure 9: Intra particle diffusion model fitted to the batch adsorption data obtained for iron (III) adsorption onto rubber seed pericarp activated carbon.

Initial Iron (III) ions Adsorption Kinetic Model Concentration (mg/l) 50 125Lagergren Pseudo First-0.032 0.044Order: $k_1 \pmod{-1} (\text{mg/g})$ 1.5453.540 R^2 0.997 0.996 Pseudo Second-Order: k_2 0.024 0.019 $(g/mg min^{-1})$ $\frac{q_e \ (\mathrm{mg/g})}{R^2}$ 1.9724.464 0.886 0.960 Intra particle Diffusion: 0.193 0.458 $K_p \ (\mathrm{mg/gmin}^{-1/2})$ \overline{C} - 0.043 0.207 \mathbb{R}^2 0.9840.967

Table 5: Lagergren pseudo first-order, pseudo second-order and intra particle constants with correlation coefficient at different initial iron (III) ions concentration.

best fit with higher correlation coefficient to describe the adsorption behaviour of iron (III) onto RSPAC.

4. Conclusions

The use of activated carbon from the pericarp of rubber seed as adsorbent material for wastewater treatment has been demonstrated to be feasible in this study. The physicochemical analysis of the abattoir wastewaters has revealed the gross pollution activities of the abattoir industry or slaughter house, hence the need for their generated wastewater to be treated. The indigenous prepared activated carbon has demonstrated that it can reduce or remove contaminants from wastewaters as effectively as commercially supplied activated carbon; hence the dependence on imported activated carbon can be discouraged, so as to conserve foreign exchange. Langmuir adsorption model could be used to describe iron (III) ions sorption equilibrium and the kinetic data of adsorption gave a better fit. The treatment is simple and economic. The kinetic data generated may be used for designing a treatment plant for iron effluents where a continuous removal or collection can be achieved on large scale.

References

- Hussain, A. A., Mohammed, S. R., Nallu, M. and Arivoli, S. Adsorption of Fe (III) from aqueous solution by acanthaceae activated carbon. *Journal of Chemical and Pharmaceutical Research*, Vol. 4, Number 4, 2012, pp. 2325-2336.
- Adesemoye A.O., Opere B.O. and Makinde S.C.O. Microbial content of abattoir wastewater and its contaminated soil in Lagos, Nigeria. *African Journal of Biotechnology*, Vol. 5, Number 20, 2006, pp. 1963-1968.

- Bull, M. A., Sterritt, R. M. and Lester, J. N. The treatment of wastewaters from the meat industry: A review. *Environmental Technology Letters*, Vol. 3, 1982, pp 117 126.
- Ezeoha, S.L. and Ugwuishiwu, B.O. Status of abattoir wastes research in Nigeria. Nigerian Journal of Technology, Vol. 30, Number 2, 2011, pp. 143–148.
- Satyanarayan, S., Ramakant and Vanerkar, A. P. Conventional approach for abattoir wastewater treatment. *Environmental Technology*, Vol. 26, Number 4, 2005, pp 441 – 448.
- Annadurai, A., Babu, S.R., Mahesh, K.P.O., Murugesan, T. Adsorption and biodegradation of phenol by chitosan-immobilized Pseudomonas putida (NICM 2174). *Bioprocess Engineering*, Vol. 2, 2000, pp. 493-501.
- Wang, S., Lin, Y. and Wai, C. M. Supercritical fluid extraction of toxic heavy metals from solid and aqueous matrices. *Separation Science and Technology*, Vol. 38, Number 10, 2003, pp 2279 – 2289.
- Okonko, I. O. and Shittu, O. B. Bioremediation of wastewater and municipal water treatment using latex exudate from Calotropis procera (Sodom Apple). *Electronic Journal of Environmental, Agricultural and Food Chemistry*, Vol. 6, Number 3, 2007, pp 1890–1904.
- Goi, D., De Leitenburg, C., Trovarelli, A. and Dolcetti, G. Catalytic wet oxidation of a mixed liquid waste: cod and aox abatement. *Environmental Technology*, Vol. 25, Number 12, 2004, pp 1397–1403.
- Agarry, S. E. and Aremu, M. O. Batch equilibrium and kinetic studies of simultaneous adsorption and biodegradation of naphthalene by orange peels immobilized Pseudomonas aeruginosa NCIB 950. *Journal* of Bioremediation and Biodegradation, Vol. 3, Number 2, 2012, pp 138-141.
- Abbasi, W.A. and Stree, M. Adsorption of uranium from aqueous solution using activated carbon. *Separation Science and Technology*, Volume 29, Number 9, 1999, pp 1217-1230.
- Baker, C. D; Clark, E. W; Jerserning, W. V., and Heuther, C. H. Removal of dissolved Organic compounds from Industrial wastewater. *Journal of Chemical Engineering Program*, Vol. 6, Number 69, 1973, pp. 77-80.
- AbdulHalim, A., Abidin, N.N.Z., Awang, N., Ithnin, A., Othman, M.S. and Wahab, M.I. Ammonia and COD remocal from synthetic leachate using rice husk composit adsorbent. *Journal of Urban and Environmental Engineering*, Vol. 5, Number 1, 2011, pp. 24 -31.
- Chaiwattananont, R., Niyomwan, N. and Noda, Y. *Optimum condition for high quality activated carbon* production from Thai raw materials. Report No 6. Thailand Institute of Scientific and Technological Research, 1998.
- Ozcan, A. and Ozcan, A. S. Adsorption of Acid Red 57 from Aqueous Solutions onto Surfactant Modified

WASTEWATER TREATMENT ADSORPTION POTENTIAL OF RUBBER SEED PERICARP-ACTIVATED CARBON 357

Sepiolite. Journal of Hazardous Material, Vol. 125, 2005, pp 252-259.

- Rengaraj, S., Moon, S. H., Sivabalan, R., Arabindoo, B. and Murugesan, V. Removal of phenol from aqueous solution and resin manufacturing industry waste water using agricultural waste: rubber seed coat. *Journal of Hazardous Material*, Vol. B89, 2002, pp 185-196.
- Vitidsant, T., Suravattanasakul, T. and Damronglerd. S. Production of activated carbon from palm oil shell by pyrolysis and steam activation in a fixed bed reactor. *Science Asia*, Vol. 25, 1999, pp. 211– 222.
- Vinod, V. P. and Anirudhan. T. S. Effect of experimental variables on phenol adsorption on Activated carbon prepared from coconut husks by single step steam pyrolysis: mass transfer process and equilibrium studies. *Journal of Science and Industrial Research*, Vol. 61, 2002, pp. 128-138.
- Ajay, K. J., Vinod, G. K., Shubhi , J. and Suhas. Removal of Chlorophenol using industrial wastes. *En*vironmental Science and Technology, Vol. 38, 2004, pp. 1195 - 1200.
- Hamad, B. K., Noor, A-Md. and Rahim. A. A. Removal of 4-chloro-2-methoxyphenol from aqueous solution by adsorption to oil palm shell activated carbon activated with K2CO3. *Journal of Physical Sciences*, Vol. 22, Number 1, 2011, pp. 39 55.
- Savova, D., Apak, E., Ekinci, E., Yardim, F., Petrof, N., Budinova, T., Razvigorova, M. and Minikora, V. Biomass conversion to carbon adsorbents and gas. *Biomass and Bioenergy*, Vol. 21, 2001, pp. 133-142.
- Cabal, B., Budinova, T., Ania, C. O., Tsyutsarski, B., Panaand, J. B. and Petrova, B., Adsorption of naphthalene from aqueous solution on activated carbons obtained from bean pods. *Journal of Hazardous Materials*, Vol. 161, 2009, pp. 1150-1156.
- Huang, C., and Huang, P. C. Application of Aspergillus oruzea and Rhizopus oryzae for Cu (II) removal. *Water Research*, Vol. 30, 1996, pp. 1985-1990.
- Cabuk, A., Ilhan, S., Fili, K. C. and Caliskan, F. Pb+2biosorption by pretreated fungal biomass. *Turkish Journal of Biology*, Vol. 29, 2005, pp. 23-28.
- Popuri, S. R., Jammala, A., Reddy, K. V. N. and Abburi, K. Biosorption of hexavalent chromium using tamarind (Tamarinddus indica) fruit shell - a comparative study. *Electronic Journal of Biotechnology*, Vol. 3, 2007, pp. 358-367.
- Mohammed, A, Nesaratnam, S. and Mohammed, H. Preparation of phosphoric acid-activated carbon using palm date pits: physico-chemcial and adsorptive properties. *Journal of Chemical Technology*, Vol. 46, Number 2, 2005, pp. 462-468.
- Amuda, S. and Ibrahim, A. O. Industrial wastewater treatment using natural material as adsorbent. *African Journal of Biotechnology*, Vol. 5, Number 16, 2006, pp 1483-1487.

- Ademuliyi, F. T., Amadi, S. A. and Amakama, N. J. Adsorption and treatment of organic contaminants using activated carbon from waste Nigerian Bamboo. *Journal of Applied Science and Environmental Man*agement, Vol. 13, Number 3, 2009, pp. 39 -47.
- Gutierrez-Sarabia, A., Fernandez-Villagomez, G., Martnez-Pereda, P., Rinderknecht-Seijas, N. and Poggi-Varaldo, H. M. Slaughterhouse wastewater treatment in a full-scale system with constructed wetlands. *Water Environmental Research*, Vol. 76, Number 4, 2004, pp. 334-343.
- Mittal, G.S. Treatment of wastewater from abattoirs before land application-a review. *Bioresource Tech*nology, Vol. 97, Number 9, 2006, pp. 1119-1135.
- Standard Test Method for Determination of Iodine Number of Activated Carbon. ASTM-D4607-94, Philadelphia, 1995.
- APHA-AWWA. Standard Methods for the Examination of Water and Wastewater. Washington D.C., U.S.A., 16th Edition, 1985, pp. 32-34.
- 33. Crisafully, R., Milhome, M.A., Cavalcante, R.M, Silveira, E.R., Keukeleire, D and Nascimento, F. Removal of some polycyclic aromatic hydrocarbons from petrochemical waste water using low-cost adsorbents of natural origin. *Bioresource Technology*, Vol. 99, 2008, pp. 4515-4519.
- Xun, Y., Shu-ping, Z., Wei, Z., Hong-you, C., Xiao-Dong, D., Xin-Mei, L., and Zi-Feng, Y. Aqueous dye adsorption on ordered malodorous carbons. *Journal* of Colloid and Interface Science, Vol. 310, 2007, pp. 83-89.
- 35. Hamad, B.K., Noor, A-Md. and Rahim, A.A. Removal of 4-Chloro-2-Methoxyphenol from aqueous solution by adsorption to oil palm shell activated carbon activated with K2CO3. *Journal of Physical Science*, Vol. 22, Number 1, 2011, pp 39–55.
- Federal Environmental Protection Agency (FEPA). Guidelines and Standards for Industrial Waste Management in Nigeria. 1988, pp. 46–55.
- 37. World Health Organization (W.H.O) Water, Sanitation and Hygiene Links to Health. 2004. Available at: www.who.int/water_sanitation-health/ publications/facts2004/en/index.html
- Baek, M.H., Ijagbemi, C.O., Se-Jin, O. and Kim, D.S. Removal of malachite green from aqueous solution using degreased coffee bean. *Journal of Hazardous Material*, Vol. 176, Number 1-3, 2010, pp 820–828.
- Singh, S. R. and Singh, A. P. Adsorption of heavy metals from waste waters on tea waste. *Global Jour*nal of Research Engineering, Vol. 12, Number 1, 2012, pp 19-22.
- 40. Das, B. and Mondal, N.K. Calcareous Soil As A New Adsorbent to Remove Lead from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Study. Universal Journal of Environmental Research and Technology, Volume 1, Number 4, 2011, pp 515-530.

- 41. Tsai, W. T. and Chen, H. R. Removal of malachite green from aqueous solution using low-cost chlorellabased biomass. *Journal of Hazardous Material*, Vol. 175, 2010, Number 1-3, pp 844–849.
- Rao, M. and Bhole, A. G. Removal of Chromium using low cost adsorbents. *Journal of American Envi*ronmental Microbiology, Vol. 27, 2000, pp. 291–296.
- Nasuha, N., Hameed, B. H. and Din, A. T. Rejected tea as a potential low cost adsorbent for the removal of methylene blue. *Journal of Hazardous Material*, Vol. 175, Number 1-3, 2010, pp 126-132.
- 44. Annadurai, G. and Krishnan, M. R. V. Adsorption of acid dye from aqueous solution by chitin: Batch Kinetic Studies. *Indian Journal of Chemical Technology*, Vol. 4, 1997, pp. 169- 172.
- Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of Ameri*can Chemical Society, Vol. 40, 1914, pp. 361-1368.
- LakshimNarayanaRao, K. C., Krishbaiah, K. and Ashutosh, A. Colour removal from a dye stuff industry effluent using activated carbon Indian. *Journal of Chemical Technology*, Vol. 1, 1994, pp. 13-19.
- 47. Sirichote, O., Innajitara, W., Chuenchom, L., Chunchit, D. and Naweekan, K. Adsorption of iron (III) ion on activated carbons obtained from bagasse, pericarp of rubber fruit and coconut shell. *Songklanakarin Journal of Science and Technology*, Vol. 24, Number 2, 2002, pp 235-242.
- Ngah, W. S. W., Ab Ghani, S. and Kamari, A. Adsorption behavior of Fe (II) and Fe (III) ions in aqueous solution on chitosan and cross-linked chitosan beads. *Bioresource Technology*, Vol. 96, 2005, pp. 443-450.
- Karthikeyon, G. and Ilango, S. S. Equilibrium sorption studies of Fe, Cu and Co ions in aqueous medium using activated carbon prepared from Recinius Communis Linn. *Journal of Applied Science and Environmental Management*, Vol. 12, Number 2, 2008, pp. 81-87.
- 50. Abasi, C. Y., Abia, A. A. and Igwe, J. C. Adsorption of iron (III), lead (II) and cadmium (II) ions by unmodified raphia palm (Raphia hookeri) fruit endocarp. *Environmental Research Journal*, Vol. 5, Number 3, 2011, pp 104 -113.
- Stephen, J. A., Mckay, G. and Khafer, K. Y. H. Equilibrium adsorption isotherm for basic dyes unto Lignite. *Journal of Chemical Technology and Biotech*nology, Vol. 45, 1989, pp. 291 - 302.
- Freundlich, H. M. F. Over the adsorption in solution. Journal of Physical Chemistry, Vol. 57, 1906, pp. 385-471.
- McKay, G., Blair, H.S, Gardner, J.R. Adsorption of dyes on chitin-I: Equilibrium studies. *Journal of Applied Polymer Science*, Vol. 27, 1982, pp. 3043-3057.
- Annadurai, G., Chellapandian , M. and Krishnan, M.R.V. Adsorption of basic dye from aqueous solution by chitosan: equilibrium studies. *Indian Journal* of Environmental Protection, Vol. 17, 1997, pp 95-98.

- 55. Treybal, R.E. *Mass transfer operation*. 10th Ed., McGraw-Hill, New York, 1988.
- Temkin, M.J. and Pyzhev, V. Recent modifications to Langmuir isotherms. *Acta Physicochim* URSS, Vol. 12, 1946, pp. 217-222.
- 57. Chen, Z., Ma, W. and Han, M. Biosorption of nickel and copper onto treated alga (Undariapinnarlifida): Application of isotherm and kinetic models. *Journal* of Hazardous Material, Vol. 155, Number 1-2, 2008, pp. 327-333.
- Moreno-Pirajan, J. C., Garcia-Cuello, V. S. and Giraldo, L. The removal and kinetic study of Mn, Fe, Ni and Cu ions from wastewater onto activated carbon from coconut shells. *Adsorption*, Vol. 17, Number 3, 2011, pp. 505-514.
- McKay, G. and Ho, Y. S. Sorption of lead (II) ions on peat. Water Research, Vol. 33, 1999, pp. 578-584.
- Lagergren, S. Zur theorie der sogenannte, adsorption geloster stoffe, Kungliga Svenska vetenskapsakademiens. *HAndlingar*, Vol. 24, 1898, pp. 1-39.
- Weber, W. J and Morris, J. C. Kinetics of adsorption on carbon from solution. *Journal of the Sanitary En*gineering Division of American Society of Civil Engineering, Vol. 89, 1963, pp. 31-60.