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Removal of Paracetamol from Aqueous Solution by Adsorption onto Activated Carbon Prepared from Rice Husk

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ABSTRACT

Removal of paracetamol from aqueous solution onto two activated carbons CANa1 and CANa2 obtained by the chemical activation of rice husk with sodium hydroxide was study in this work. The characterization of the activated carbons showed that the ph at zero charge was 6.80 for CANa1 and 6.54 for CANa2, while the pH of CANa1 was 7.10 and that of CANa2 was 7.13. from the adsorption of acetic acid, the specific surface areas were obtained as 178.13 m^2/g for CANa1 and 104.82 m^2/g for CANa2. The determination of the iodine number gave values 528.39 mg/g and 494.67 mg/g for CANa1 and CANa2 respectively. The kinetics of the adsorption was adequately described by the pseudo-second order and intraparticulate diffusion models. Concerning the equilibrium studies, the model of langmuir described best the adsorption on CANa1 while the model of freundlich described best the adsorption on CANa2. From the results obtained, CANa1 and CANa2 constitute effective adsorbents for the elimination of paracetamol from industrial waste water, the equilibrium is in according with the langmuir model, while the quantities adsorbed were 20.964 mg/g and 14.881 mg/g respectively.

Keywords: Paracetamol; Adsorption; Activated carbon; Chemical activation

Abbreviations: CANA1: activated carbon obtained by chemical activated of rice husk with NaOH as activating agent at 500°C**;** CANa2: activated carbon obtained by chemical activated of rice husk with NaOH as activating agent at 450°C

INTRODUCTION

The lack of appropriate treatment systems for effluents from pharmaceutical industries is responsible for introducing significant amounts of medicines into diverse aquatic ecosystems, thus creating serious environmental problems throughout the world. The production of pharmaceuticals has increased rapidly in the last decades, providing better health quality for humans and animals [1]. The presence of these pharmaceuticals in the environment in concentrations in the µg/L or ng/L range poses the threat to aquatic organisms in terms of mutagenicity as well as currently unknown effects to humans. Pharmaceuticals originally from humans and feedstock wastewaters often found their way into surface water sources [2]. Among the drugs frequently used in the world; analgesics and anti-inflammatories are the most common, and they are widely consumed with or without medical prescription. Of these drugs, paracetamol stands out as being highly toxic to the liver, and it has a high potential for developing hepatitis [3]. Paracetamol; an antipyretic/analgesic drug has been widely investigated because of its common use and because

of the fact an overdose of it results in health problems such as acute hepatic failure, liver damage [4,5,6,7] and even death.

To prevent the release of pharmaceuticals from industries into natural water sources, a number of conventional methods for the removal of organic pollutants are being investigated. These methods may be divided into three main categories: physical, chemical and biological. Often, in drug poisoning, the amount of drugs in the order of magnitude of many grams may have been ingested. This amount is close to the adsorption capacity of the activated carbons often used. As standard treatment, a dose of 50 g activated carbon has been shown to be effective as a gastro-intestinal decontaminant in human volunteers who ingested multiple drugs, although these investigations involved only sub-toxic drug [8-11]. Adsorption, one of the physical methods is generally considered to be an effective method for quickly lowering the concentrations of organic molecules in an effluent [12]. The activated carbons have been previously used to remove lead from aqueous effluents. The most important commercial adsorbent is a carbonaceous material with a large surface area, high porosity, adequate pore size distribution and high mechanical strength [13]. Activated carbons can be produced from different carbonaceous materials such as coal, wood, peat and agricultural wastes especially lignocellulosic by-products like pinewood [14], date's stone [15], cola nut shells [16], and maize stalks [17]. Recent progress of industrial technologies provides new application fields for activated carbons in super-capacitors, and the carbons are required to have the desired pore structure [18]. The production of activated carbon from agricultural by-products has potential economic and environmental benefits. It converts unwanted, low value agricultural waste to useful, high value adsorbents. Activated carbons are increasingly being used to remove organic compounds and heavy metals of environmental and/ or economic concern [16] from waste streams.

The aim of this study was to use rice husk; a local agricultural waste, to produce activated carbons, and to investigate the removal of paracetamol from aqueous solution using these activated carbons.

MATERIALS AND METHODS

Preparation of activated carbon

The rice husk used in this work was collected from Ndop subdivision in the North-West Region of Cameroon. The rice husk was washed with tap water, then rinsed with distilled water to eliminate impurities and then dried under sunlight for 72 hours before activation.

The ratio of impregnation is defined as the ratio of the mass of the activating agent to the mass of the dry biomass precursor. To produce an activated carbon with an impregnation ratio of 35%, 200 g of dried rice husk was put in contact with 350 mL of a 1.0 molar solution of NaOH. The mixture was kept for 30 minutes for activation to take place before being dried in an oven set at 105°C for 24 hours. The samples of impregnated rice husk were carbonized for 1 hour at 450°C and 500°C, at a heating rate of 5°C/min. The activated carbons obtained were labeled CANa1 for rice husk carbonized at 500°C and CANa2 for rice husk carbonized at 450°C. The carbonization was carried out in an electric furnace of mark ISUNU, which has an automatic regulation, and a temperature programmer coupled to it. The various activated carbons thus obtained were dried for 24 hours at the temperature of 105°C, before being crushed and filtered to obtain activated carbon of particles of sizes lower than 100 µm.

Characterization of adsorbents

Bulk density:

A 15 cm^3 specific gravity bottle was weighed empty, and later when carefully filled to the mark with powder activated carbon. The difference in the masses gave the mass of the powder activated carbon. The bulk density was calculated from the equation:

$$\text{bulk density} = \frac{\text{weight of powder}}{15} \qquad (1)$$

Moisture content

A previously weighed crucible was weighed with 1 g of powdered air dried activated carbon. It was then placed on a hot plate maintained at 110 $^{\circ}$C. After one hour, it was taken out and cooled in a desiccator before being weighed again. The ratio of the mass of the powder lost to its original mass gave the moisture content of the sample.

Iodine number

To gain further knowledge of the porous structure of activated carbon, the adsorption of iodine from liquid phase was adopted by other researchers in the characterization of sludge-based activated carbons [19,20]. The adsorption of aqueous I_2 is considered a simple and quick test for evaluating the microporosity of activated carbons associated with pore diameter less than 2 nm. The iodine number, defined as the amount of iodine adsorbed per gram of

activated carbon at an equilibrium concentration of 0.02 N, was measured according to the procedure established by the American Society for Testing and Materials [20]. Activated carbon of mass 0.1 g, was mixed with 30 mL of 0.02 N iodine solutions and stirred for 3 hours. After filtration, 10 mL of the filtrate was titrated against 0.005 N sodium thiosulphate solution using starch as indicator.

Surface area

Another method of determining the specific surface area of adsorbent is based on adsorption of molecules of acetic acid [21], whose molecular surface area of 21 $Å^2$ is close to that of nitrogen, N_2 (16.2 $Å^2$). To determine the specific surface area of the adsorbent, 20 ml of acetic acid solution of concentration ranging between $4x10^{-3}$ and $8x10^{-3}$ M was put in contact with 0.1 g of activated carbon. This mixture was filtered after agitating for 60 minutes. The residual concentration of the acid was determined by the volumetric assay technique [21]. The specific surface area S_L (in m^2/g) was determined using the equation (2):

$$S_L = Q_m N S_A \qquad (2)$$

Where N = $6.02x10^{23}$ mol^{-1} (Avogadro constant), S_A = 21 $Å^2$ (molecular surface area of acetic acid) and Q_m maximum quantity of acid adsorbed as obtained from the isotherm of Langmuir.

Batch adsorption

Adsorption experiments were carried out by mechanical agitation at room temperature. For each run, 20 mL of paracetamol solution of known initial concentration (between 70-120 mg/L) was treated with a known weight of different activated carbon. After agitation, the solution was filtered, and the filtrate analyzed to obtain the residual of concentration paracetamol by using the UV/Vis spectrophotometer (Jenway, model 6715). Similar measurements were carried out by varying adsorbent doses, pH of the solution, ionic strength and the initial concentrations of the solution. The percentage removal (%R) of paracetamol, and the amount (Q_e) of paracetamol adsorbed were calculated using the following expressions:

$$\%R = \frac{(C_0 - C_t)}{C_0} x100 \qquad (3)$$

$$\%R = \frac{(C_0 - C_t)}{m} xV \qquad (4)$$

C_0 is the initial concentration of the phenol, C_e is its equilibrium concentration, C_t is the concentration of the paracetamol solution at the time t, V is the volume of the solution, and m is the mass of the absorbent.

Effect of contact time

To determine the effect of agitation time on the adsorption process, 0.1 g of ground adsorbent was agitated in a 20 mL solution of paracetamol of initial concentration 100 mg/L for different time intervals. At each time t, the solution was rapidly filtered and the residual concentration determined by spectrophotometer. The amount (Q_e) of paracetamol adsorbed was calculated by using equation (4).

Effect of amount of adsorbent

In this set of experiments, different masses of the adsorbents ranging between 0.025 to 0.45 g were treated with 20 mL solution of the paracetamol of initial concentration 100 mg/L.

Effect of initial pH

For each adsorbent, the optimal mass of adsorbent obtained at the end of the preceding study was treated with 20 mL of aqueous solution of 100 mg/L of paracetamol in the pH range of 2.0 – 3.5. The adjustment was done by adding either HCl or NaOH.

Kinetics of adsorption studies

The kinetics experiments were conducted using a series of 20 mL solutions containing known amounts of adsorbent and concentrations of paracetamol. The solutions were vigorously agitated for increasing time intervals. At the end of each interval, the solution was analyzed in order to determine the residual concentration of paracetamol. A number of kinetic models were used to test the fit of the experimental data. These are:

The pseudo-first order model

The pseudo-first order equation is generally expressed as [22,23]:

$$\frac{dQ_t}{dt} = K_1(Q_e - Q_t) \qquad (5)$$

Where Q_e and Q_t are the adsorption capacities at equilibrium and at time t, respectively (in mg/g) and K_1 is the rate constant for the pseudo-first order adsorption (1/min).

After integration and applying boundary conditions that at t = 0, Q_t= 0; and at t = t, $Q_t = Q_t$, the integrated form of equation (5) becomes:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \qquad (6)$$

The pseudo-second order model

The pseudo-second order chemisorption kinetic equation [24,25] is expressed as Equation 7:

$$\frac{dQ_t}{dt} = K_2(Q_e - Q_t)^2 \qquad (7)$$

Where K_2 is the rate constant for the pseudo-second order adsorption (g/mg.min).

For boundary conditions are that, at t = 0, Qt= 0; and at t = t, Qt = Qt, the integrated and rearranged form of equation (7) is:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \qquad (8)$$

In the equation (8), $K_2 Q_e^2 = h$ is the initial rate for the adsorption

Intraparticle diffusion model

The intra-particle diffusion model or the Weber and Morris equation [26] models the type of diffusion mechanism involved in adsorption processes. It is given here by equation (9):

$$P = K_{id} t^a \qquad (9)$$

Where K_{id} is the intra-particle diffusion constant (mg/g.min). The linear form of this equation takes the following form [27].

$$lnP = lnK_{id} + alnt \qquad (10)$$

Where; P is the percentage of paracetamol removed at instant t and a is a constant that depends on the adsorption mechanism. When intra-particle diffusion plays a significant role in controlling the kinetics of the sorption process, the plots of $\ln P = \ln t$ yield straight lines passing through the origin and the slope gives the rate constant, K_{id}. However, when the transport of the solute molecules from the liquid phase up to the solid phase boundary plays the most significant role in adsorption, the liquid film diffusion model may be applied.

Batch equilibrium experiments

For each run, the adsorbent was mixed with 20 mL solution of paracetamol at different initial concentrations from 50-110 mg/L. The suspension was stirred for 60 minutes with different activated carbon. The amount of paracetamol adsorbed at equilibrium, Qe (mg/g) was calculated using equation (4). Equilibrium data were then fitted by using the isotherms of Langmuir, Freundlich, Dubinin-Radushkevich and Temkin.

The Langmuir isotherm:

The Langmuir adsorption isotherm is often used of the equilibrium of the adsorption of solutes from solutions. It is expressed as [28]:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \qquad (11)$$

Where, Q_e is the adsorption capacity at the equilibrium solute concentration, (in mg of adsorbate per g of adsorbent); C_e is the equilibrium concentration of adsorbate in solution (mg/L), while Q_m is the maximum adsorption capacity corresponding to complete monolayer coverage expressed in mg of solute adsorbed per g of adsorbent. K_L is the Langmuir constant in L of adsorbate per mg of adsorbent, and it is related to the energy of adsorption. Equation (11) can be rearranged in the linear form:

$$\frac{C_e}{Q_e} = \frac{1}{kQ_m} + \frac{C_e}{Q_m} \qquad (12)$$

The factor of separation of Langmuir, RL, which is an essential factor characteristic of this isotherm is calculated by using the relation [29]:

$$R_L = \frac{1}{1+K_L Q_m C_0} \qquad (13)$$

Where C0 is the higher initial concentration of paracetamol, while K_L and Qm are the Langmuir constant and the maximum adsorption capacity respectively. The parameters indicate the shape of the isotherm as follows: RL values indicate the type of isotherm. when RL = 1 adsorption is linear; when 0 < RL< 1, it is favourable, when RL = 0, it is irreversible, while to be unfavorable, while when RL> 1, it is unfavorable.

The Freundlich isotherm:
The Freundlich isotherm is based on adsorption on a heterogeneous surface, and it is expressed as [30].

$$Q_e = FC_e^{1/n} \qquad (14)$$

Where F and n are empirical constants. By taking logarithms on both sides, the equation gives the more convenient linear form:

$$lnQ_e = lnK_f + \frac{1}{n} lnC_e \qquad (15)$$

A linear graph of ln Qe versus ln Ce gives the values of 1/n and ln Kf.
The $1/n$ values indicate the type of isotherm as follows: to be irreversible $1/n = 0$; to be favorable $0 < 1/n < 1$, while to be unfavorable $1/n > 1$.

The Temkin isotherm:
The isotherm of Temkin developed in 1941 [31] for an adsorption in gas phase was transposed to the liquid phase by Zarrouki in 1990 [32]. The isotherm of Temkin was generally presented by the following equation:

$$\frac{Q_e}{Q_m} = \frac{RT}{\Delta Q} \ln(AC_e) \quad (16)$$

Where $\frac{Q_e}{Q_m}$ is the rate of covering the surface of the adsorbent, A is the constant of balance and ΔQ is the variation of the energy of adsorption. The linear form of the equation (16) is:

$$Q_e = Q_m \frac{RT}{\Delta Q} lnA + Q_m \frac{RT}{\Delta Q} ln(C_e) \qquad (17)$$

The value of Q_m is obtained from the equation of Langmuir.

The Dubinin-Radushkevich isotherm:
Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption. The Dubinin-Radushkevich isotherm is commonly used to describe the sorption isotherms of single solute systems. The Dubinin-Radushkevich isotherm, apart from being an analogue of the Langmuir isotherm, is more general than Langmuir isotherm because it does not apply to the homogeneous surfaces or surfaces of constant adsorption potential. The Dubinin-Radushkevich isotherm is expressed as [33].

$$Q_e = Q_m exp[\frac{(RTln\left(1+\frac{1}{C_e}\right))^2}{-2E_a^2}] \qquad (18)$$

Where, E_a is the main energy of adsorption and gives information about the physical and chemical features of adsorption. The linear form of the Dubinin-Radushkevich isotherm equation is:

$$lnQ_e = lnQ_m - K'\varepsilon^2 \qquad (19)$$

Where, $\varepsilon = RTln\left(1+\frac{1}{C_e}\right)$ is called the Polanyi potential.

RESULTS AND DISCUSSION

Characterization of activated carbons

The physicochemical properties of the adsorbents as obtained in this work after their characterization are shown in table 1.

Table 1: Characterization of adsorbents

Adsorbent	Bulk density (kg/m^3)	Moisture Content (%)	pH	pH_{pcz}
CANa1	655.53	7	7.1	6.8
CANa2	645.33	9.09	7.13	6.54

Iodine number:

Iodine number is defined as the number of milligrams of iodine absorbed by one gram of activated carbon powder. Table 2 gives the values of the iodine number of the samples. The iodine numbers of activated carbons prepared in this investigation lie between 490.00-530.00. Generally, the higher the iodine number, the greater the sorption capacity. ASTM D 4607 describes the procedure of determining the iodine number. The iodine number recommended as a minimum by the American Water Works Association for a carbon to be used in removing low molecular weight compounds is 500. The two factors that determine good iodine number are activation temperature and raw materials. This suggests that surface area increases in terms of microscopic pores. Iodine adsorption is usually associated with micro pores because of the small size of iodine molecule.

Surface area: The specific surface area of an adsorbent is its surface area per unit of mass. From Table 2, it can be observed that the specific surface area of CANa1 is higher than that of CANa2. Since CANa2 was obtained at 450°C and CANa1 was obtained at 500°C, it implies that increasing the temperature of carbonization increases the development of pores.

Table 2: Iodine number and surface area values of the samples

Samples	Iodine number(mg/g)	Surface area(m^2/g)
CANa1	528.39	178.13
CANa2	494.67	104.82

Fourier transform infrared spectroscopy

From figure 1, the presence of either a free O-H or alcohol is depicted by the broad band between 3200 cm^{-1} and 3600 cm^{-1}. The vibration band at 3352 cm^{-1} was attributed to the presence of acetylenic stretching. The adsorption band 1631.35 cm^{-1} is attributed to quinonic, monosubstituted alkene and carboxylate structures mean while the adsorption band at 1724.52 cm^{-1} is attributed to a carboxylic tautomeric structure (C=O). The precursor from rice husks contain C-N, C=N, due to vibrations around 1630-1730 cm^{-1}. The C-O single bond adsorptions at about 1033 cm^{-1}. It also has peaks around the range from 2858 cm^{-1} to 2925.66 cm^{-1}, which indicate the existence of symmetric -CH_3, -CH_2 stretching groups. Strong stretching vibration+ at 3352.11 cm^{-1} may correspond to the acetylenic C-H bonds. Aliphatic nitro compounds (N-O) are present at 1373.56 cm^{-1} could be allocated to halogeno-alkanes vibrations between 400 cm^{-1} and 800 cm^{-1}.

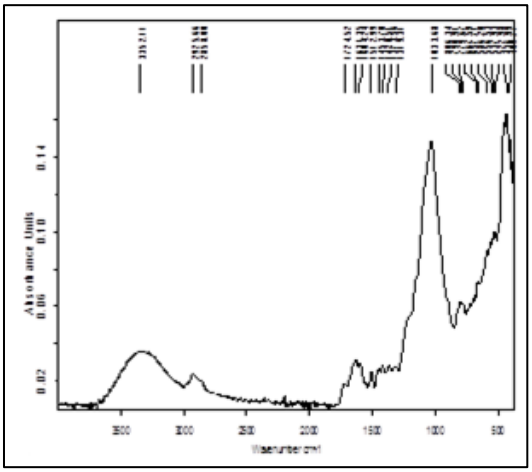

Figure 1: FTIR spectra of rice husks

The FTIR spectra of the activated carbons treated with sodium hydroxide at different temperatures are shown in figure 2. The bands present in the IR spectrum of activated carbon are: 1694.74, 1566.55, 1371.14, 1067.32, 789.27, 452.28, 415.77, 386.96 cm^{-1}. Absorption band between 1700 – 1650 cm^{-1} with maximum at 1694.74 cm^{-1} is attributed to C=O bond stretching of the carboxylic anhydride groups. The peak observed at 1566.55 cm^{-1} is attributed to the carbonyl functional group. The shoulder at 1371.14 cm^{-1} can be ascribed to N-O stretching of aliphatic nitro compounds of the activated carbon derived from sodium hydroxide activation. The absorption band at 900 – 1070 cm^{-1} can be attributed to C–O groups of esters or ethers. The band between 600–400 cm^{-1}corresponds to C-H bond vibrations in the aromatic ring.

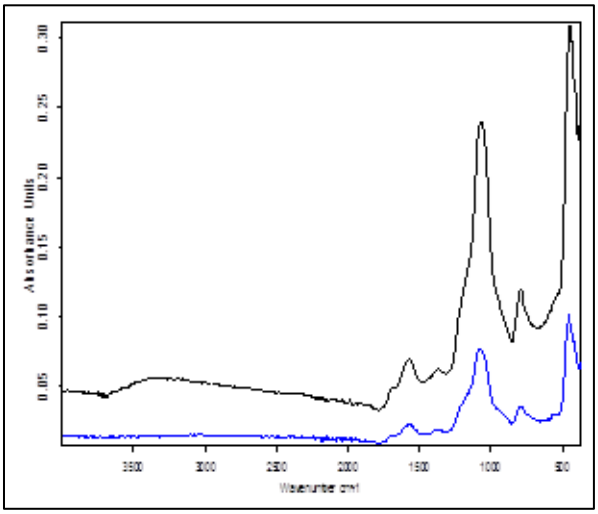

Figure 2: FTIR spectra of CANa1 (a) and CANa2 (b)

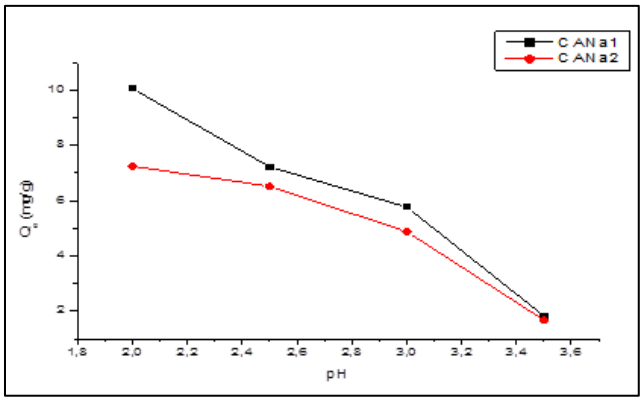

Figure 3: The effect of pH solution on uptake of the paracetamol onto activated carbon

Effect of contact time:

Figure 4 presents the effect of contact time on the adsorption of paracetamol. In the figure, it is observed that adsorption takes place at a very fast rate during the first 20 minutes. This is followed by a slower rate of adsorption up to 100 minutes before equilibrium is attained. Furthermore, a large fraction of the total amount of paracetamol was removal within a very short time. In the first stage, the sorbate molecules are being adsorbed onto a surface where there are no other such molecules already attached, and consequently the sorbate-sorbate interactions are negligible [36]. Therefore, paracetamol molecules reach the adsorption sites easily. The second part of the curve shows that as time progresses, the number of free sites on the activated carbon decreases, and the non-adsorbed molecules are assembled at the surface, thus limiting the capacity of adsorption.

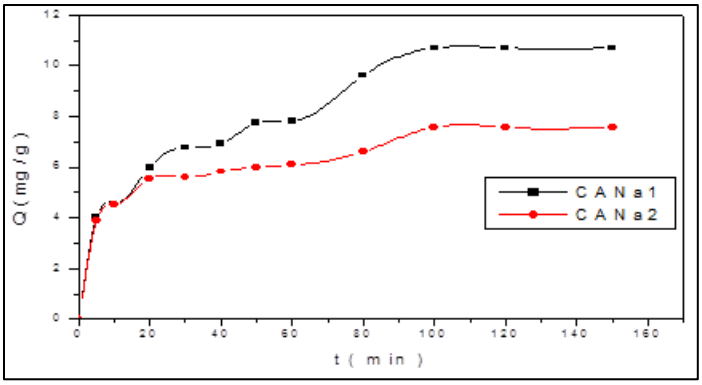

Figure 4: Effect of agitation time on the adsorption of paracetamol onto activated carbon

Effect of adsorbent dose

In this part of the experiment, different masses of the adsorbent were stirred with paracetamol solution of constant initial concentration 100 mg/L for 100 minutes. The results show that the percentage adsorption increases with adsorbent mass (figure 5). This is explained by the fact that increasing the mass of adsorbent leads to an increase in the number of adsorption sites on the surface of the adsorbent. It should be noted that adsorbent CANa1 has the greater percentage of elimination than CANa2. The percentage of elimination is 53.01 and 48.55 for CANa1 and CANa2 respectively. This implies that percentage adsorption increases with the increase in surface area, and this too depends on the number of pores. That is the greater the surface area, the greater the number of pores, and the number of pores increases with an increases in the carbonization temperature.

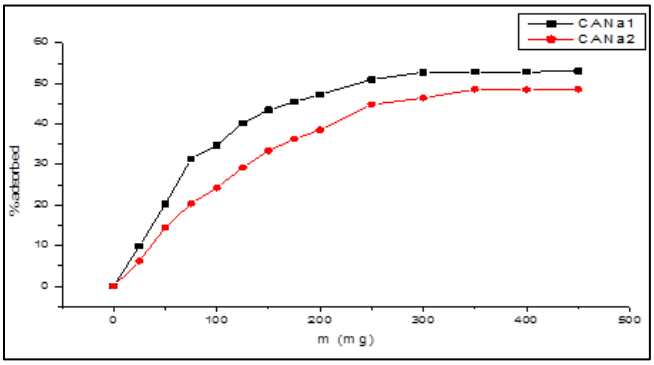

Figure 5: Effect of adsorbent mass on paracetamol adsorption onto activated carbon

Kinetic study

Modeling of kinetic data is important for the industrial application of the adsorption process, because it gives information that can be used to compare different adsorbents under different operating conditions [37]. The kinetic models used to investigate and describe the adsorption of paracetamol are the pseudo-first order, pseudo-second order, and intra particular diffusion models. The plots of the kinetic models are presented in figures 6 to 8. The validity of the order of adsorption process is based on the regression coefficients, R^2 and on the predicted values of Q_e. The parameters for the kinetics models are presented in table 3.

Table 3: Parameters of kinetic models for paracetamol adsorption on CANa1 and CANa2

Model	Parameters	CANa1	CANa2
Pseudo first order	R^2	0.917	0.926
	Q_e(mg/g)	7.775	3.407
	K_1 (1/min)	0.021	0.015
pseudo-second order	R^2	0.976	0.987
	Q_e (mg/g)	12.345	8.13
	K_2 (g/min.mg)	0.0036	0.01
	h (mg/min.g)	0.549	0.661
Intraparticle diffusion	R^2	0.976	0.965
	K_{id} (min^{-1})	5.72	10.601
	a (mg/g)	0.314	0.196

The results show that the first and second order correlation coefficient, R^2, for these studies are greater than 0.92. Consequently, these adsorption data may be assumed to follow the first and second order mechanisms in the early stages of the adsorption process. It is often incorrect to apply simple kinetic models such as first or second order rate equations to an adsorption with solid surfaces, because they are rarely homogeneous and the effects of transport phenomena and chemical reactions are often experimentally inseparable [38]. In the multiple first order kinetics adsorption process, the first stage is attributed to the binding or anchorage of paracetamol molecules with the active spots on the solid surface by removal and reorganization of the surface-bound originally adsoerded. The second stage is attributed to the denaturation and reorganization of the activated carbon of the interface, leading to the formation of spread films [39]. Atuna and Sismanoghu [40] reported that in the case of two kinetics steps, the first step of adsorption was more rapid than the second, and the adsorption rate was controlled by either a film diffusion or intraparticule diffusion.

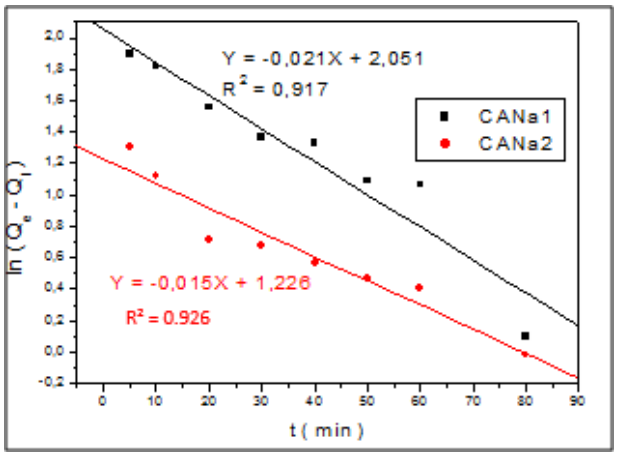

Figure 6: Linearized pseudo-first order plots

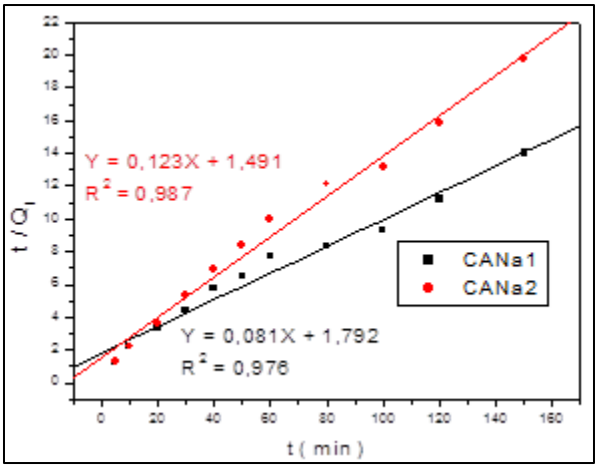

Figure 7: Linearized pseudo-second order plots

Adsorption isotherms

The Langmuir, Freundlich, Dubinin-Radushkevich and Temkin models have been used in this study. The adsorption isotherms relate the amount of paracetamol adsorbed at equilibrium Q_e (mg/g) to the paracetamol concentration at equilibrium, C_e (mg/L) and the plots are given in figures 9 to 12. The parameters of the adsorption isotherm are shown in table 4.

In comparing the values given in table 4 above, one realizes that the coefficients of correlation obtained are higher than 0.9 for the studied models. This suggests that the equilibrium of the adsorption of paracetamol on the activated carbons from rice husks is adequately represented by the models of Langmuir, Freundlich, or Temkin and Dubinin-Radushkevich.

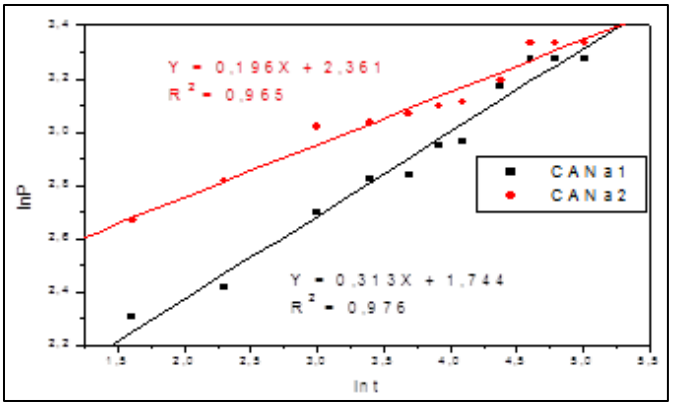

Figure 8: Linearized Intraparticle diffusion plots

Table 4: Isotherm parameters for paracetamol uptake from aqueous solution

Models	Parameters	CANa1	CANa2
Langmuir	Q_{max}(mg/g)	20.964	14.881
	K_L (L/mg)	0.0143	0.0085
	R_L	0.0328	0.0732
	R^2	0.9951	0.9826
Freundlich	1 /n	0.5035	0.5656
	K_F (L/g)	1.2299	0.5042
	R^2	0.9947	0.9928
Temkin	ΔQ (kJ/mol)	10.0049	10.1399
	K_T	0.1081	0.2979
	R^2	0.9949	0.9875
Dubinin-Radushkevich	Q_{max} (mg/g)	15.9028	9.9721
	E (kJ/mol)	3.1403	3.7164
	R^2	0.9932	0.9822

According to the correlation coefficient (R^2), the adsorption of paracetamol by CANa1 is better described by the model of Langmuir while that of CANa2 is better described by the model of Freundlich. The model of Langmuir shows a distribution of the paracetamol molecules in the form of monolayer adsorption on a homogeneous surface. Using the maximum capacities of adsorption of activated carbon obtained and starting from the Langmuir model, it is possible to classify them according to their performances: CANa1 (Q_{max} = 20.964 mg/g) are more effective than CANa2 (Q_{max} = 14.881 mg/g). According to equation 13, the values of R_L obtained from both adsorbents are range between 0 and 1 (table 4). This range, ($0 < R_L < 1$) shows that the process of adsorption is favorable for the two adsorbents. The values of 1/n of the model of Freundlich are lower than 1 suggesting that the process of fixing of paracetamol on the adsorbent is chemisorption. According to the Temkin isotherm, (i) the heat of adsorption of all molecules in the layer decreases linearly with surface coverage due to adsorbent-adsorbate interaction, and (ii) adsorption is characterized by uniform distribution of energy [41,42]. Based on the energies, the variation of energy of adsorption ΔQ (kJ/mol) resulting from the linearization of the Temkin model is positive. A positive value of ΔQ means that the process of adsorption is exothermic. According to the Temkin model the adsorption energies obtained are 10.005 and 10.140 kJ/mol for CANa1 and CANa2 respectively; values which are less than 40 kJ/mol. From the Dubinin-Radushkevich model the adsorption energies are 3.140 and 3.716 kJ/mol onto CANa1 and CANa2 respectively, also less than 8 kJ/mol. These observations (values of energies) suggest that physical adsorption dominates the adsorption process.

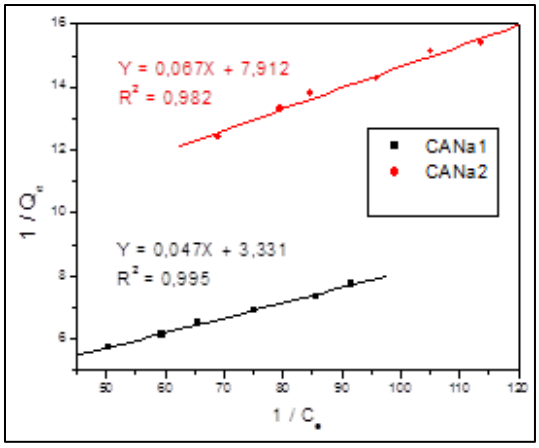

Figure 9: Linear plot of the model of Langmuir

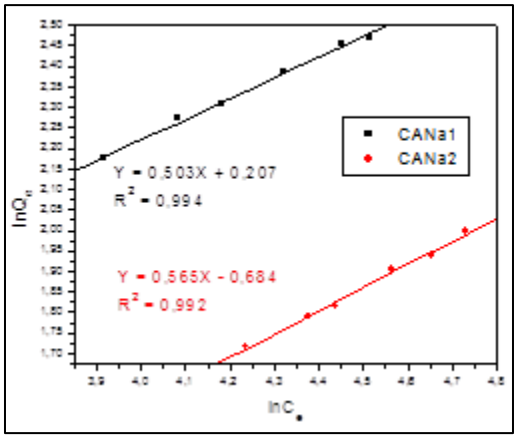

Figure 10: Linear plot of the model of Freundlich

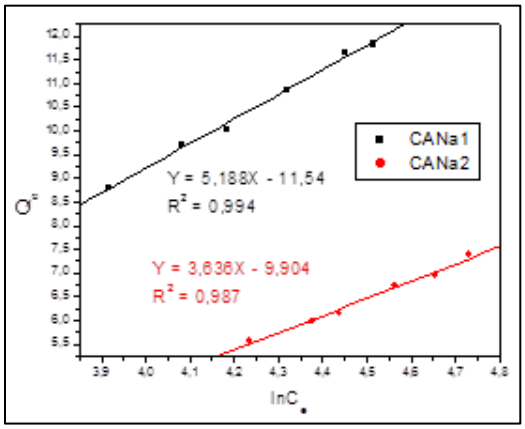

Figure 11: Linear plot of Temkin

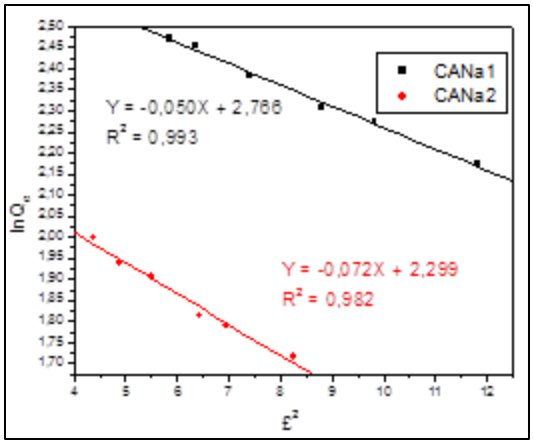

Figure 12: Linear plot of Dubinin-Radushkevich

CONCLUSION

In this work, the potential of two activated carbons, obtained from rice husks by chemical activation using NaOH, for the removal of paracetamol from aqueous solutions was established. The investigation revealed that the quantity of paracetamol adsorbed increases with the increase in the initial concentration of paracetamol and contact time between the adsorbent and paracetamol solution. Maximum adsorption took place at pH=2 for both adsorbents. Using the same adsorbent mass of 450 mg, the percentage eliminations were recorded as 52.87 and 48.56 respectively for CANa1 and CANa2. The kinetic model of pseudo-second order described better the adsorption of paracetamol by both materials. As for the equilibrium the study, isotherm of Langmiur described better the adsorption of paracetamol on CANa1 while CANa2 was best described by the Freundlich. These results suggest the competition between physisorption and chemisorption during the adsorption of paracetamol on these activated.

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