

Kinetics and equilibrium studies of adsorption of phenol in aqueous solution onto activated carbon prepared from rice and coffee husks

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Abstract— Activated carbons obtained from the chemical activation of rice and coffee husks using H_3PO_4 were used to remove phenol from aqueous solution. Batch adsorption experiments were carried out and the amount of phenol adsorbed was determined as a function of adsorption time, pH of solution, adsorbent mass and initial concentration of phenol. The activated carbon used as adsorbent was characterized for its moisture content, bulk density, CHNS analysis, pH of zero point charge (pH_{zpc}) and pH of the phenol solution. Some kinetics parameters were calculated; from kinetic results, the initial rate (obtained by pseudo second order) of adsorption is greater for all the adsorbent. The applicability of pseudo-second order model showed that the rate limiting step was chemisorption, involving forces caused by sharing or exchange of electrons between sorbent and sorbate. An Equilibrium study of the adsorption process showed that Langmuir isotherm described the isotherm data with high correlation coefficients on CAH2 and CAMH, while that of Temkin described that on CAH1. The values of energy obtained from the Temkin isotherm are also positive, this show that the adsorption process is exothermic. The results indicate that chemical rice husk and coffee husk activated carbon is suitable to be used as an adsorbent for phenol adsorption from aqueous solutions.

Index Terms— activated carbon, adsorption, coffee husk, phenol, rice husk.

I. INTRODUCTION

Phenol and phenolic derivatives are organic chemicals that appear very frequently in waste water from almost all heavy chemical, petrochemical and oil refining industries [1]. Large amounts of waste water are usually generated during the manufacturing and processing of organic chemicals. The concentration of these organic materials in waste water usually exceeds the level for safe discharge into the environment. Phenol and its derivatives are toxic and

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carcinogenic in nature and are among the primary environmental pollutants [2].

To send these large volumes of industrial effluents into the environment, the concentration of the pollutants must be drastically lowered to acceptable levels.

Another source of environmental pollution is residues obtained from agricultural activities. These wastes accumulate on the farms and on refuse dumped from agricultural processing industries. The increasing demand for food due to the increasing world population means that the waste materials generated from these activities can no longer be neglected. Agro industries processing coffee and rice are important examples. Coffee and rice husks are generated by these industries in large quantities. Appropriate means of disposing them must be sort.

Conventional methods for the removal of organic pollutants in effluents may be divided into three main categories: physical, chemical and biological [3]. 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 [4].

Activated carbon, the most important commercial adsorbent, is a carbonaceous material with a large surface area, high porosity, adequate pore size distribution and high mechanical strength [5], [6]. Activated carbons can be produced from different carbonaceous materials such as coal, wood, peat and agricultural wastes especially lignocellulosic by-products like pinewood [7], dates' stone [8], cola nut shells [9], maize cobs [10]. Recent progress of industrial technologies provides new application fields for activated carbons in super-capacitors and, at the same time requires the carbons having a desired pore structure [11].

The production of activated carbon from agricultural by-product has potential economic and environmental impacts. It converts unwanted, low value agricultural waste to useful, high value adsorbents. Activated carbons are increasingly being used in water to remove organic compounds and heavy metals of environmental and/ or economic concern [9] from waste streams.

The aim of this study is to use rice husk, a local agricultural waste, to produce activated carbon. After producing the activated carbon, the kinetic and equilibrium aspects of the removal of phenol onto these activated carbon will be investigated.

II. MATERIALS AND METHOD

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 the impurities and then dried in the sun 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. The washed rice husk was impregnated using the above ratio. To produce an activated carbon with an impregnation ration of 75%, 20 g of dried rice husk was put in contact with 35 g of a solution of H₃PO₄ of concentration 1M. The mixture was allowed 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 products obtained from the calcination were washed with distilled water until there were no phosphate ions detected any more in the water when tested with lead nitrate. The activated carbons obtained were labeled CAH1 obtained from rice husk at 500°C; CAH2 obtained from rice husk at 450°C; and CAMH obtained at 500°C by mixing 12 g of rice husk with 8 g of coffee husk. The experimental setup used is an ISUNU mark electric furnace with automatic regulation, having the temperature programmer relied to the furnace. 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 size lower than 100 µm.

Characterization of adsorbents

- Bulk Density

A 25 cm³ 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:

$$\text{Bulk density} = \frac{\text{weight of powder}}{25} \quad (1)$$

- Moisture content

A previously weighed crucible was weighed with 1g of powder, air dried activated carbon. It was then placed on a hot plate maintained at 110°C it was taken out, cooled in a desiccator before being weighed again. The ratio of the mass lost by the powder to its original mass gave the moisture content of the sample.

- CHNS elemental analysis

CHNS elemental analysis provide a means for the rapid determination of carbon, hydrogen, nitrogen and sulphur in organic matrices and other types of materials. They are capable of handling a wide variety of sample types.

- Iodine number

To gain further knowledge of the porous structure of activated carbon, iodine adsorption from liquid phase was adopted by other researchers [12] in the characterization of sludge-based activated carbons. The adsorption of aqueous I₂ is considered a simple and quick test for evaluating the surface area of activated carbons associated with pores less than 2 nm. The iodine value, 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 (ASTM) [13]. 0.1 g of activated carbon was mixed with 30 mL of 0.02 N iodine solutions, stirred for 3 hours and then the contents filtered. 10 mL of the filtrate was titrated against 0.005 N sodium thiosulphate solution using

starch as indicator until a clear solution was observed.

- Batch Adsorption

Adsorption experiments were carried out by mechanical agitation at room temperature. For each run, 20 mL of phenol of known initial concentration (between 50-110 mg/L) was treated with a known weight of different activated carbon. After agitation for the appropriate length of time, the solution was filtered, and the filtrate analyzed to obtain the concentration residual phenol by using the UV/Vis spectrophotometer (Jenway model 6715). Similar measurements were carried out by varying adsorbent doses, pH of the solution, and the initial concentrations of the solution. The percentage removal (%R) of phenol and the amount (Q_e) of phenol adsorbed were calculated using the following expressions:

$$\%R = 100 \frac{C_0 - C_t}{C_0} \quad (2)$$

$$Q_e = \frac{C_0 - C_e}{m} V \quad (3)$$

C₀ is the initial concentration of the phenol, C_e is its equilibrium concentration, C_t is the concentration of the phenol solution at the time t, V is the volume of the solution, and m is the mass of the adsorbent.

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 phenol of initial concentration 70 mg/L for different time intervals. At each time, the solution was rapidly filtered and the residual concentration determined by spectrophotometer. The percentage removal (%R) of phenol was calculated by using Equation (2).

Effect of amount of adsorbent

In this set of experiments, different masses of the adsorbents ranging between 0.25 to 2.0 g were treated with 20 mL solution of the phenol of initial concentration 70 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 70 mg/L of phenol, in the pH range of 2.0 – 7.0.

Kinetics of adsorption studies

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

The pseudo-first order model:

The pseudo-first order equation is generally expressed as [14]:

$$\frac{dQ}{dt} = K_1(Q_e - Q_t) \quad (4)$$

Where Q_e and Q_t are the adsorption capacity at equilibrium and at time t, respectively (in mg/g) and K₁ is the rate constant for the pseudo-first order adsorption (L/min).

After integration and applying boundary conditions at $t = 0$, $Q_t = 0$; and at $t = t$, $Q_t = Q_t$, the integrated form of equation (4) becomes:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (5)$$

The pseudo-second order model:

The pseudo-second order chemisorption kinetic equation (Ho and McKay) [15] is expressed as Equation 6:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad (6)$$

Where q_e and q_t are the adsorption capacity (mg/g) at equilibrium, and at time t , respectively and K_2 is the rate constant for the pseudo-second order adsorption (g/mg.min). For boundary conditions at $t = 0$, $q_t = 0$;

and at $t = t$, $Q_t = Q_t$, the integrated and rearranged form of equation (6) is:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (7)$$

The Elovich kinetic equation

The Elovich equation is generally expressed as [16]:

$$\frac{dQ_t}{dt} = \alpha e^{-\beta Q_t} \quad (8)$$

Where Q_t is the sorption capacity at time t (mg/g), α is the initial adsorption rate (mg/g.min), and β is the desorption rate constant (mg/g.min) during any one experiment.

The integrated and simplified equation (assuming that $\alpha\beta t \gg 1$) is:

$$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (9)$$

Intraparticle diffusion model

The rate of adsorption is known to be controlled by several factors including the following [17]:

Diffusion of solute from the solution to the film surrounding the adsorbent particle;

Diffusion through the film to the particle surface;

Diffusion from the particle surface to the internal sites on the adsorbent particle;

Uptake of solute on the solute surface, and this could involve several mechanisms such as physicochemical sorption, ion exchange, complexation or precipitation.

One type of equation used to model the intraparticle diffusion was developed using the concept of linear driving force. It is expressed as [18], [19]:

$$Q_t = X_i + K^1 t^{0.5} \quad (10)$$

X_i is the boundary layer diffusion effect, and it depicts the boundary layer thickness, while K^1 is the initial rate of adsorption (mg/g.min), and it is controlled by intra-particle diffusivity.

Batch equilibrium experiments

For each run, the adsorbent was mixed with 20 mL solution of dye at different initial concentrations from 50-110 mg/L. The suspension was stirred for 60 minutes with different activated carbon. The amount of dye adsorbed at equilibrium, Q_e (mg/g) was calculated using equation (2):

$$Q_e = \frac{(C_0 - C_t)V}{m} \quad (3)$$

Where, C_0 and C_t are the initial and equilibrium concentrations of phenol, V the volume of the solution, and m

the adsorbent mass. Equilibrium data were then fitted by using the isotherm Langmuir, Freundlich, Elovich 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 [20]:

$$Q_e = Q_m \frac{K_L C_e}{1 + K_L C_e} \quad (14)$$

Where, Q_e is the adsorption capacity at the equilibrium solute concentration, in the 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 (14) can be rearranged in the linear form:

$$\frac{1}{Q_e} = \frac{1}{Q_m K C_e} + \frac{1}{Q_m} \quad (15)$$

The factor of separation of Langmuir, R_L , which is an essential factor characteristic of this isotherm is calculated by using the relation [21]:

$$R_L = \frac{1}{1 + K Q_m C_0} \quad (16)$$

Where C_0 is the higher initial concentration of methyl orange, while K_L and Q_m are the Langmuir constant and the maximum adsorption capacity respectively. The parameters indicate the shape of isotherm as follows:

R_L values indicate the type of isotherm: to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavourable ($R_L > 1$).

The Freundlich Isotherm

The Freundlich isotherm is based on adsorption on a heterogeneous surface, and it is expressed as [22]

$$Q_e = F C_e^{1/n} \quad (17)$$

Where Q_e is the quantity of solute adsorbed at equilibrium, also called adsorption density; it is expressed in mg of adsorbate per g of adsorbent; C_e is the concentration of adsorbate at equilibrium, F and n are empirical constants. By taking logarithms on both sides, the equation gives the more convenient linear form:

$$\ln Q_e = \ln F + \frac{1}{n} \ln C_e \quad (18)$$

The Temkin Isotherm

The isotherm of Temkin developed in 1941 for an adsorption in gas phase was transposed to the liquid phase by Zarrouki in 1990 [23]. The isotherm of Temkin was generally presented by the following equation:

$$\theta = \frac{RT}{\Delta Q} \ln K_0 C_e \quad (19)$$

Where $\theta = \left(\frac{Q_e}{Q_m}\right)$ is the rate of covering of the surface of the adsorbent, K_0 is the constant of balance and ΔQ is the variation of the energy of adsorption. The linear form of the equation of Temkin is:

$$Q_e = \frac{Q_m RT}{\Delta Q} \ln K_0 + \frac{Q_m RT}{\Delta Q} \ln C_e \quad (20)$$

The value of Q_m which one introduces into this degree of covering is given starting from the equation of Langmuir.

The Elovich isotherm

This isotherm differs from that of Langmuir about the evolution of the sites of adsorption. The number of site available varies in this model in an exponential way during adsorption, which implies an adsorption in several layers. The Elovich isotherm is described by the relation [19]:

$$\frac{Q_s}{Q_m} = K_\epsilon C_s \exp\left(\frac{Q_s}{Q_m}\right) \tag{21}$$

K_ϵ : is the constant of balance of Elovich (L/mg)

Q_m : maximum capacity of Elovich

The linear form of the isotherm of Elovich is given by:

$$\ln\left(\frac{Q_s}{C_s}\right) = \frac{Q_s}{Q_m} + \ln K_\epsilon Q_m \tag{22}$$

III. RESULTS AND DISCUSSIONS

Characterization of Activated Carbons

The physicochemical properties of the adsorbents as obtained in this work after their characterization are shown in tables 1 & 2.

The elemental analysis of rice husk and activated carbon are listed in table 2. The results show that the quantities of element decreases when the temperature of activation increases. These is in accordance with the volatile matters like CO, CO₂, CH₄, aldehydes, and so forth.

Iodine number

Iodine number is defined as the number of milligrams of iodine absorbed by one gram of activated carbon powder. Table 3 gives the values of the iodine number of the samples. The iodine numbers of activated carbons prepared in this investigation lies between 476 -600. 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 dwell time. 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.

ADSORPTION STUDIES

Effect of contact time

Figure 1 presents the effect of contact time on the adsorption of phenol. In the figure, we observe a fast adsorption during the first ten minutes, followed by a slower rate of adsorption up to 60 minutes when equilibrium is attained. This implies that the adsorption proceeds in two phases: the first one is characterized by high adsorption rate and this is due to the fact that initially, the number of adsorbent sites available on the activated carbon is higher. Therefore, phenol molecules reach the adsorption sites easily. The second part shows that when 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.

In fact, the interactions $\pi-\pi$ affect the adsorption rate. The

presence of attracting groups of electrons tends to attract the electrons of the π -systems in carbon. $\pi-\pi$ interaction is usually the mean mechanism involved in phenol adsorption. The maximum quantities adsorbed in equilibrium are 8.56, 8.68 and 9.56 mg/g respectively for CAH1, CAH2 and CAMH leading to a percentage of 64.46, 66 and 72.91%.

Effect of adsorbent dose.

In this part of the experiment, different masses of the adsorbent were stirred with phenol solution of constant initial concentration 70 mg/L for 60 minutes. The results show that the percentage of adsorption increases with adsorbent mass (fig 2). This is explained by the fact that increase in the mass increases the number of sites of adsorption on the surface of adsorbent. It should be noted that adsorbent CAMH has the greatest percentage of elimination than the two others. The capacity of adsorption (expressed as a percentage) increase from 20.13 to 83.81, 20.11 to 86.00 and 28.46 to 88.39 for CAH1, CAH2 and CAMH respectively when the mass increases from 25 to 200 mg.

Table 1: Characterization of Adsorbents

Adsorbent	Bulk density (kg/m ³)	Moisture Content (%)	pH	pH _{pez}
CAH1	802	8.86	5.20	3.0
CAH2	826	6.93	6.30	3.45
CAMH	744	8.91	3.72	2.30

Table 2: Elemental analyses of rise husk and activated carbon prepared from rice hush

Adsorbent	%C	%H	%N	%S	Reference
Rice husk	38.7	5.0	0.7	0.1	[24]
CAH1	37.26	1.71	0.44	0	This work
CAH2	38.12	1.57	0.43	0	This work
CAMH	49.21	1.80	1.44	0	This work

Table 3: Iodine number values of the samples

Samples	Iodine number
CAH1	476.25
CAH2	495.3
CAMH	590.55

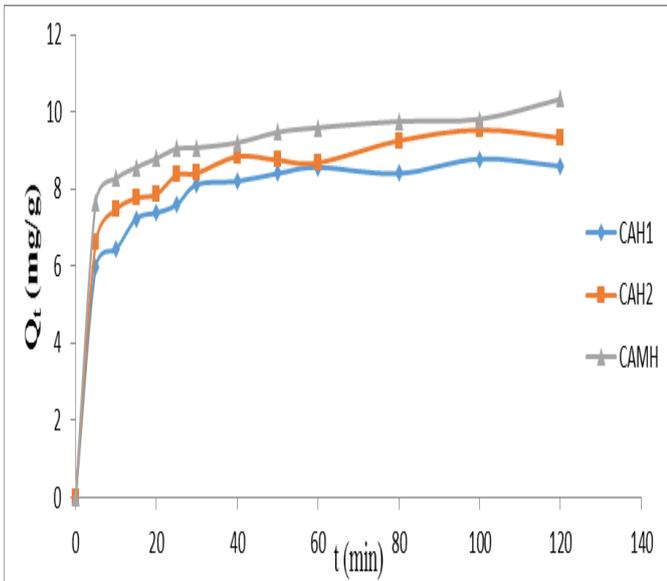


Figure 1: The effect of contact time on the amount of phenol onto different activated carbon (initial concentration of 70 mg/L, ambient temperature, pH = 2, m = 0.1 g)

Effect of pH

The pH of solution is one of the most important parameters affecting phenol adsorption process because it affects the surface charge of the adsorbent as well as the degree of ionization and speciation of phenol². The adsorbed quantities of phenol slowly decreases with the increase in the pH for values at the top of 2 for the adsorbent CAH1 and CAH2. But the opposite effect is observed for adsorbent CAMH. The maximum phenol uptake obtained at low pH can be explained by the fact that at this pH range, the adsorbent surface is charged positively and the phenol is protonated; this creates a strong electrostatic interaction between phenol molecule and the carbon surface [25].

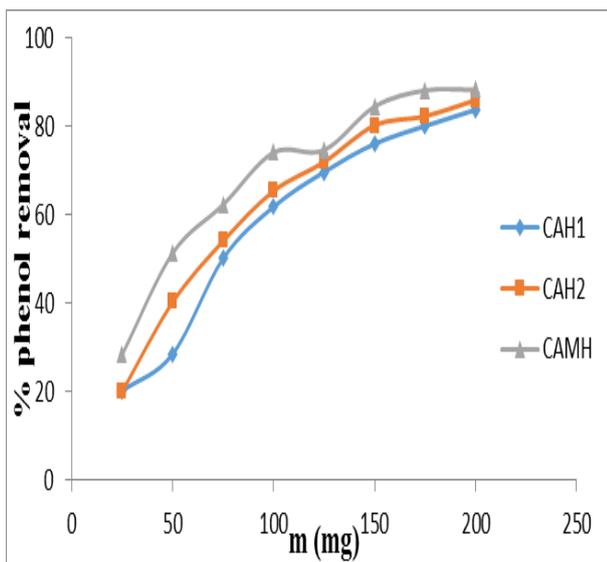


Figure 2: Effect of the mass of activated carbon on the removal of phenol from aqueous solution (initial concentration = 70mg/L, ambient temperature, t = 60 min, pH = 2)

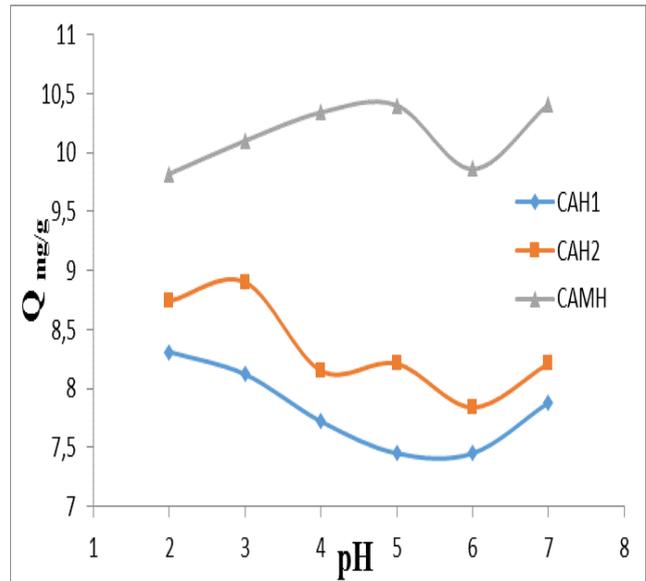


Figure 3: The effect of pH solution on uptake of the phenol onto activated carbon (initial concentration = 70mg/L, ambient temperature, t = 60 min, m = 0.1 g)

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 for removing pollutant wastewater [26]. The kinetic models used to investigate and describe the adsorption of phenol are the pseudo-first order, pseudo-second order, Elovich, intra-particle Elovich and intra particular diffusion models. The plots of the kinetic models are presented in figures 4 to 7

The validity of the order of adsorption process is based on the regression coefficients and on predicted Q_e values. The parameters for the kinetics models are presented in table 4.

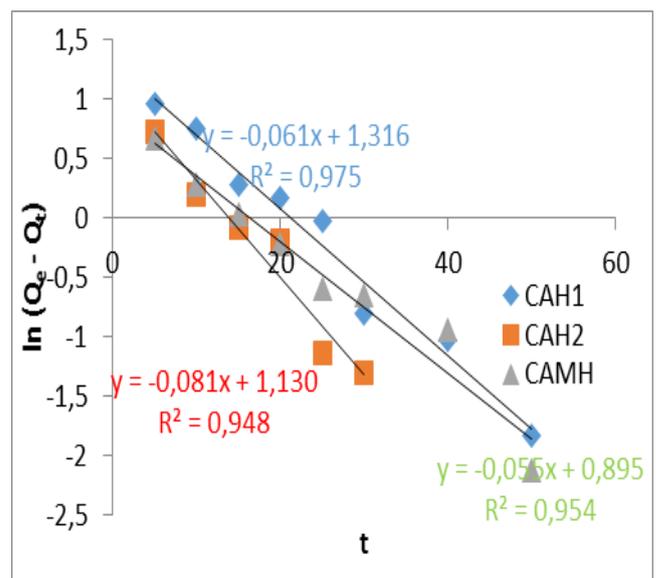


Figure 4: Linearized pseudo-first order plots

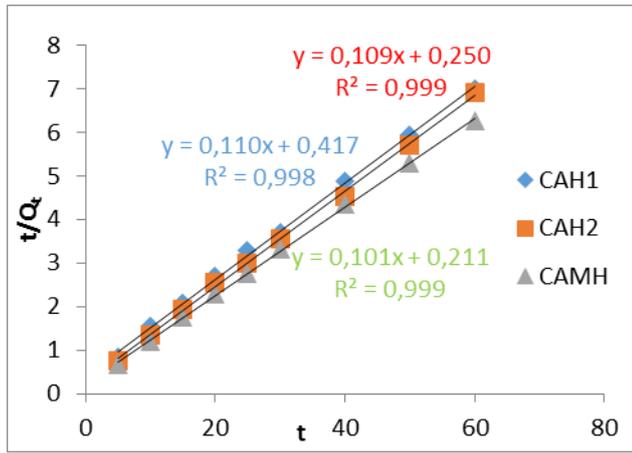


Figure 5: Linearized pseudo-second order plots

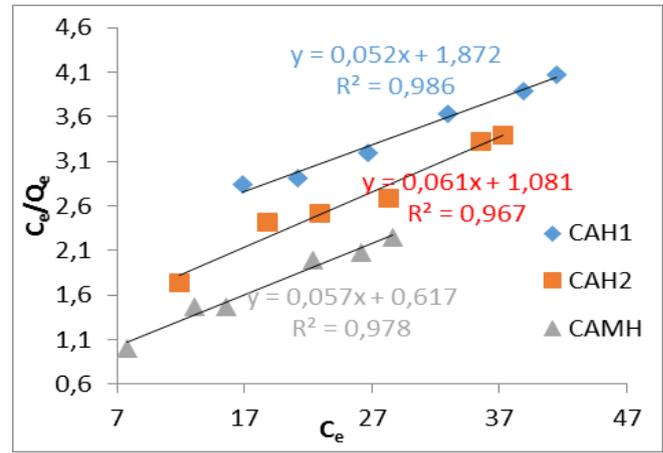


Figure 7: Linear plot of the model of Langmuir

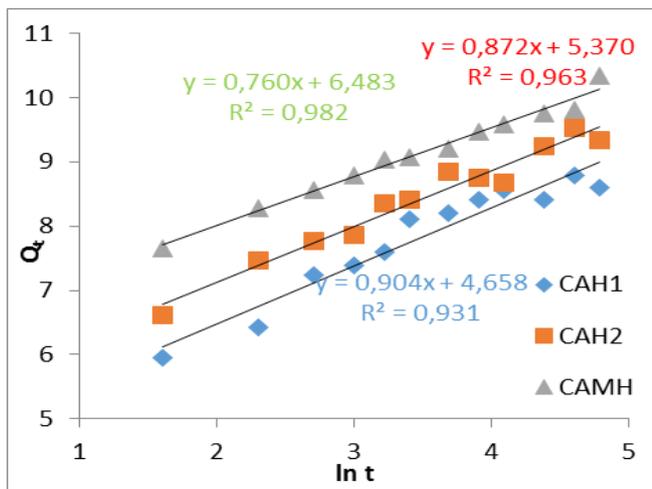


Figure 6: Linearized Elovich plots

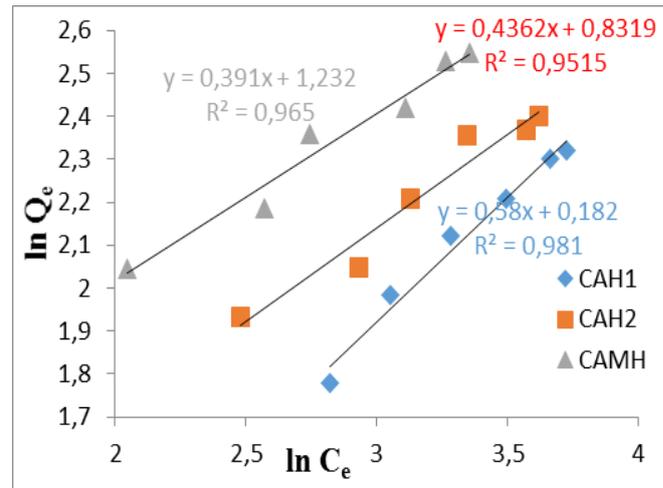


Figure 8: Linear plot of the model of Freundlich

It can be noted that the pseudo-second order kinetics give the highest value of correlation coefficients as compared to those given by the pseudo-first order, Elovich and intraparticle diffusion models. Secondly, all the kinetic models have high correlation coefficients ($R^2 > 0.900$).

Table 4: Parameters of kinetic models for phenol adsorption on CAH1, CAH2 and CAMH

Adsorbents		CAH1	CAH2	CAMH
Pseudo first order	K_1 (1/min)	0.061	0.081	0.895
	Q_e (mg/g)	3.728	3.096	2.447
	R^2	0.975	0.948	0.954
Pseudo second order	K_2 (g/min.mg)	0.029	0.046	0.048
	Q_e (mg/g)	9.091	9.174	9.901
	h	2.398	4.000	4.739
	R^2	0.998	0.999	0.999
Elovich	β	1.106	1.146	1.316
	α	156.31	412.39	3851.29
	R^2	0.931	0.963	0.982
Intraparticle diffusion	K_{id} (1/min)	0.476	0.374	0.327
	X_i	5.136	6.192	7.199
	R^2	0.937	0.866	0.939

The high values of correlation coefficients and the negligible deviation between the various models make it difficult to be categorical about which kinetic model fits best.

In the table 3, the only clear conclusion is that, both physical and chemical adsorptions equally participate in the overall process of phenol adsorption onto these three activated carbons. The correlation coefficients close to the unit in all cases (pseudo –second order). These indicate that the adsorption of phenol from aqueous solution on these three samples obey the pseudo-second order kinetic model. The applicability of the pseudo-second order model shows that the rate limiting step is chemisorption involving forces caused by sharing or exchange of electrons between sorbent and sorbate. In the intraparticle diffusion model plots for the adsorption of phenol onto CAH1, CAH2 and CAMH, the straight line do not pass through the origin indicating that the intraparticle diffusion is not the only process that can control kinetics of adsorption [27], [28]

Adsorption Isotherms

The Langmuir, Freundlich, Elovich and Temkin models have been used in this study. The adsorption isotherms relate the amount of solute adsorbed at equilibrium Q_e (mg/g) to the phenol concentration at equilibrium, C_e (mg/L) and the plots are given in figures 7 to 10. The parameters of the adsorption isotherm are shown in table 5.

The correlation coefficients of adsorption are quite high for all the models. The coefficient of adsorption of Langmuir

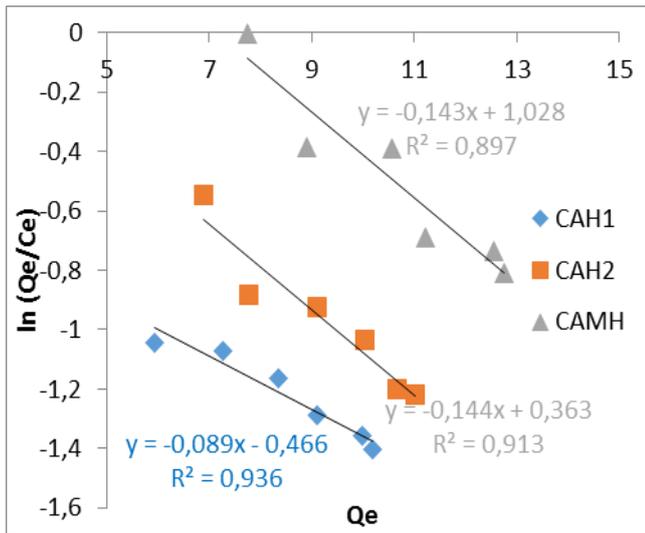


Figure 9: Linear plot of Elovich

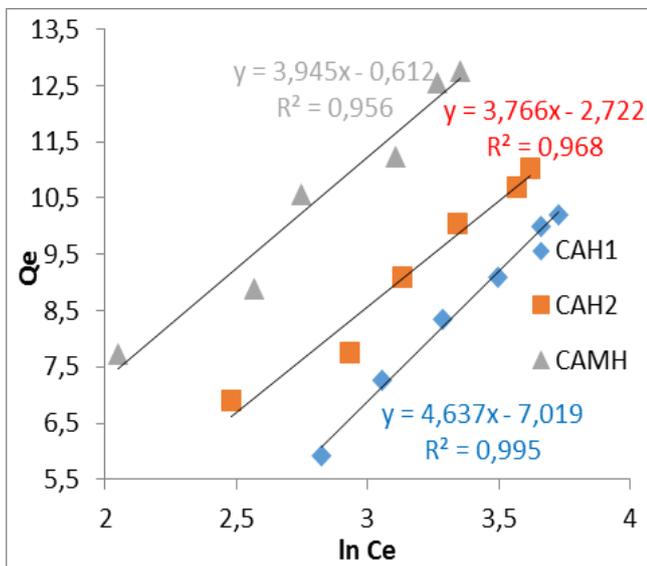


Fig10: Linear plot of Temkin

is higher for CAH2 and CAMH than the others. This shows that the model of Langmuir describes better the phenomena of adsorption on the surface of these two adsorbents. However with CAH1, the coefficient of correlation of linear transform of Temkin is highest. The value of $1/n$ for CAMH is smaller than that of CAH1 and CAH2, which once more testifies the high adsorption capacity of this adsorbent with respect to both others. The value of the average energy of adsorption for the three adsorbents is positive, which means that the adsorption process is exothermic.

The factor of separation R_L of Langmuir which is an essential factor characteristic of its isotherm is calculated by relation [29]:

$$R_L = \frac{1}{1 + K_L Q_m C_0} \quad (23)$$

The values of R_L obtained from all the adsorbents are ranging between 0 and 1 (table 5). The range, ($0 < R_L < 1$) shows that the process of adsorption is favorable for the three adsorbents²⁴.

Table 5: Isotherm parameters for phenol uptake from

aqueous solutions

Adsorbents		CAH1	CAH2	CAMH
Langmuir	K_L	0.028	0.056	0.924
	Q_e (mg/g)	19.23	16.39	17.54
	R^2	0.986	0.967	0.978
	R_L	0.0197	0.01165	0.0007
Freundlich	K_F	1.200	2.296	3.428
	$1/n$	0.580	0.436	0.391
	R^2	0.981	0.951	0.965
Elovich	K_E	0.056	0.021	0.399
	Q_e (mg/g)	11.236	6.944	6.993
	R^2	0.936	0.913	0.897
Temkin	ΔQ (KJ/mol)	10.275	10.783	11.016
	K	0.220	0.485	0.856
	R^2	0.995	0.968	0.956

IV. CONCLUSION

In this work, the potential of three activated carbons obtained from rice and coffee husks by chemical activation using H_3PO_4 as low cost adsorbents for the removal of phenol from aqueous solutions was established. The present investigation revealed that the quantities of phenol adsorbed increases with the increase in the initial concentration of phenol and contact time between the adsorbent and phenol solution. Maximum adsorption took place at pH=2 for all other adsorbents. The percentage eliminations 83.81, 86.00 and 88.39 respectively were recorded for CAH1, CAH2 and CAMH for the same adsorbent mass of 0.2g. The sorbent/sorbate equilibrium was well described by the pseudo-second order kinetic model and CAH1 by Temkin adsorption model, while CAH2 and CAMH were better describe by Langmuir's adsorption model.

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REFERENCES

- [1] Maarof H.L., Hameed B.H. & Ahmed, "Adsorption isotherm for phenol onto activated carbon". *AJChE*, **4** (1), 70-76, (2004)
- [2] Bohli T., Fiol N., Villaescusa I. & Ouedemi A. "Adsorption on activated carbon from olive stones: kinetic and equilibrium of phenol removal from aqueous solution". *J. Chem. Eng. Process. Technol.*, **4** (6), 1-5, (2013)
- [3] Hao O.J., Kim H. Chiang P.C. "Decolorization of wastewater", *Crit. Rev. Environ. Sci. Technol.*, **30**, 449-505, (2000).
- [4] Tsai W.T., Lai C.W., Su T.Y. (2006), Adsorption of bisphenol-A from aqueous solution onto minerals and carbon adsorbents. *J. Har. Mat.*, **B 134**, 169-175.
- [5] Tancredi N., Medero N., Möller F., Piriz J., Plada C., Cordero T. "Phenol adsorption onto powdered and granular activated carbon prepared from eucalyptus wood". *J. Col. Interf. Sci.*, **279**, 357-363, (2004)
- [6] Mohanty K., Das, D. & Biswas M.N. "Adsorption of phenol from aqueous solutions using activated carbon prepared from tectona grandis swadust by $ZnCl_2$ activation". *Chem. Eng. J.*, **115**, 121-131, (2005)

- [7] Tseng R.L., Wu F.C., Juang R.S. "Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons". *Carbon*, **41**, 487-495, (2003)
- [8] Yahia A.A. "Activated carbon from dates' stone by ZnCl₂ activation". *Eng.Sci.*, **17**(2), 75-100, (2006)
- [9] Yuan C.S., Lin H. Y., Wu C.H. & Liu M.H. "Preparation of sulfurized powdered activated carbon from waste tires using an innovative composite impregnation process". *J. Air & Waste Manage. Assoc.*, **54**, 862-870. (2004).
- [10] Dina D.J.D., Ntieche A.R., Ndi J.N. and Ketcha M. J. (2012), Adsorption of acetic acid onto activated carbons obtained from maize cobs by chemical activation with zinc chloride (ZnCl₂). *Res. J. Chem. Sci.* **2** (9), 42-49.
- [11] Menéndez -Díaz, J.A. & Martín-Gullón I. "Types of carbon adsorbents and their production". *Activated Carbon Surfaces in Environmental Remediation*, 1-45, (2006)
- [12] Martín M.J., Artola A., Balaguer M.D. and Rigola M., "Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions". *Chem. Eng. J.*, **94**(3), 231-239, (2003)
- [13] Ndi J.S., Ketcha J.M., Anagho S.G., Ghogomu J.N. and Bilibi E.P.D. "Physical and chemical characteristics of activated carbon prepared by pyrolysis of chemically treated cola nut (cola acuminata) shells wastes and its ability to adsorb organics". *Int. J. Adv. Chem. Technol.*, **3**(1), 1-13, (2014)
- [14] Anagho S.G., Ketcha J.M., Tchoufon T. D. R. & Ndi J.N., "Kinetic and equilibrium studies of the adsorption of mercury (II) ions from aqueous solution using kaolinite and metakaolinite clays from Southern Cameroon". *Int. J. Res. Chem. Env.* **3**, 1-11, (2013)
- [15] Ketcha, J. M. and Bougo, T. C., "Removal of mercury (II) ions from aqueous solutions using granular activated carbon (GAC) and kaolinite clay from Mayouom in Cameroon: kinetics and equilibrium studies". *Res. J. Chem. Env.*, **14** (3), 60-65, (2010)
- [16] Gaid A.; Kaoua F.; Mederres N. & Khadjia M. "Surface mass transfer processes using activated date pits as adsorbents". *Water SA*, **20** (4), 273-278, (1994)
- [17] Igwé, J. C. and Abia, A. A., "Adsorption kinetics and intraparticle diffusivities for bioremediation of Co(II), Fe(II), Cu(II) ions from water using modified and unmodified maize cob". *J. Phys. Sci.*, **2** (5), 119-127, (2007)
- [18] Tchoufon T.D.R., Anagho S.G., Njanja E., Ghogomu J.N., Ndifor-Angwafor N. G. & Kamgaing T. "Equilibrium and kinetic modelling of methyl orange adsorption from aqueous solution using rice husk and egussi peeling". *Int. J. Chem. Sci.*, **12**(3), , 741-761, (2014)
- [19] Volesky B. "Sorption and Biosorption". *BV Sorbex Inc, Montreal-St.Lambert*, Quebec, Canada, 315 P, (2003).
- [20] Kannan, N. and Sundaram, M. M., "Kinetics and mechanism of removal of Methylene blue by adsorption on various carbons- A comparative study". *Dyes and Pigments*, **51**, 25-40, (2001)
- [21] Ebner A.D., Ritter J.A. and Novratil, J.D. "Adsorption of Cesium, Strontium and Cobalt ions on magnetite and a magnetite-silica composite". *Ind. Eng. Chem. Res.*, **40**, 1615-1623, (2001).
- [22] Saifuddin, N.N. and Raziah A.Z. "Removal of heavy metals from industrial effluent using *Saccharomyces cerevisiae* (bakers' yeast) immobilized in chitosan/Lignosulphonate matrix". *J. Appl. Sci. Res.*, **3** (12), 2091-2099, (2007)
- [23] Hamdoui O. & Naffrechoux E. "Etude des équilibres et de la cinétique d'adsorption du cuivre (II) sur des particules réactives dans un réacteur fermé, parfaitement agité et thermostaté". *Labanese Sci. J.*, **6**(1), 59-68, (2005)
- [24] Subhashree P. "Production and characterization of activated carbon produced from a suitable industrial sludge". *Projet report, National Institute of Technology Rourkela*, pp 32-33. (2011)
- [25] Lü G., Hao J., Liu L., Ma H., Fang Q. "The adsorption of phenol by lignite activated carbon". *Chinese. J. Chem. Eng.*, **19**, 380-385, (2011)
- [26] Ho Y.S., Porter J.F. & McKay G. Equilibrium isotherm studies for the adsorption of divalent metals ions onto peat: copper, nickel and lead single component systems. *Water, Air and Soil pollut.* **141**, 1-33, (2002)
- [27] Srihari V. and Das A. "The kinetic and thermodynamic studies of phenol-sorption onto three agro-based carbons". *Desalination*, **255**, 220-234, (2008)
- [28] Hall K.R., Eagleton L.C. Acrivos A. and Vermeulen T. "Pore and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions". *Ind.Eng.Chem.Fund.*, **5**, 212-223.(1996)
- Zahra H., Mohammed A. S., Zurina Z. A., Ahmadun F. R. & Mohd H. S. I. "Removal of methyl orange from aqueous solution using dragon fruit (*Hylocereus undatus*) foliage". *Chem. Sci. Trans.* **2** (3), 900-910. (2013)**