



## The Relation Between Adsorption Resistances During Removal of Colour in Sugar Mill Effluent



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### Abstract

Phenolic compounds are the major source of colour in sugar mill effluent. Details mechanism of diffusional resistances for removal of phenolic compounds namely: phenol, 2-4 dichlorophenol and 2-4 dinitrophenol by adsorption onto activated carbon rice husk (ACRH) was studied. The mechanism studied was based on three diffusional resistance models: external mass transfer, intraparticle diffusion and twin resistance mass transfer. The relationship of mass transfer coefficient versus time shows that the adsorption process follows two regimes started with high mass transfer and then low mass transfer, due to high diffusion from bulk to surface of ACRH particles then slow mass transfer into pores of ACRH. The comparison between the three models was followed up by using the relationship of mass transfer coefficient versus time ( $ka c^n$ ).

It was found that adsorption of phenol in the intraparticle structure is 180% higher than adsorption on the external surface of the ACRH. The value of mass transfer coefficient of the twin resistance model is close to that of external mass transfer model and both are lower than that of intraparticle diffusion model. The experimental results proved that intraparticle diffusion is controlling step. Moreover, three adsorption isotherms were studied: Langmuir, Freundlich and Dubinini -Roduch (D-R) for the three phenolic compounds.

**Keywords:** mass transfer, two resistances, single resistance, phenolic compounds, activated carbon, adsorption.

### 1. Introduction

The sugar industry is characterized by consuming large amount of water consequently, discharge huge amount of waste water. The water requirement for sugar industry is 1-5 m<sup>3</sup>/ton of sugar cane and generates 0.4-1 m<sup>3</sup> waste water per ton of sugar cane [1] and [2]. Waste water from sugar industry is characterized with high BOD (5000-17000 ppm), high COD (2000-8000 ppm) and its colour between pale yellow and brown [3]. Colouring materials in sugar are soluble compounds and represents one of the most impurities in sugar industry. Sugar colourants are not single molecules species and consist of a wide range of materials each with its molecules weight, pH sensitivity and chemical structure [4].

Sugar refineries in sugar industries generate a highly coloured effluent resulting from the

regeneration of anion exchange resin [5].

This effluent causes environmental problem due to its high organic load, intense colour and presence of phenolic compounds [5]. Colourants in sugar effluent according to Godshall [4] can be divided into two general categories: Colorant produced by degradation of hexoses those naturally present in sugar cane, such as pigments and phenolic compound that can form high molecular weight during processing. Godshell [4] also pointed out that phenolic acids and other phenolic compounds present in sugar cane play an important role in sugar colour formation. Poly phenol react, in presence of iron and oxygen to form dark colour compounds [4]. Treatment of sugar industry waste water was mostly carried out by anaerobic and/or aerobic treatment. However, oil and grease are not easily degraded and cause a serious problem [3]. Recently adsorption technique was aroused

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considerable interest. Commercial activated carbon proved the most effective material for controlling the organic load and colour from sugar industry effluent. However, due to high cost of commercial activated carbon and about 10-15 % loss during regeneration different low cost materials as adsorbent for sugar mill waste water were used with great successes [6], [7] and [8]. Phenolic compounds are preferentially adsorbed on the surface of ashes [10]. Rice husk (RH) is a byproduct from rice mill industry has high percentage of ashes about 25% [9]. Annual global product of rice is 759.6 million tons. Around 20% of rice paddy is husk this means that 152 million tons rice husk waste per year [10]. RH is an abundant bio-waste with low combustible value and cause damage to the environment (solid waste) can bring the issue of its sustainable utilization. RH is mainly composed of lignin (20-30%), hemicellulose (55-60%), silica (15-20 %) and extracts (2-5%) which can be regarded as a natural organic -inorganic composite [9].

Adsorption of adsorbate on an adsorbent from aqueous phase go through three steps:

- 1- Transport of adsorbate from bulk solution to the adsorbent surface.
- 2- Adsorption of adsorbate on the external surface of the adsorbent.
- 3- Internal diffusion of adsorbate into the pores of the adsorbent.

The slowest of the above steps will control the process or will be the rate limiting step. It is assumed that first step is rapid when compared with the other two steps and can be neglected, especially in well agitated solid / liquid absorber [11]. Therefore, the prediction of adsorption rate limiting step is an important aspect for the study and design the adsorption process.

The aim of this study is to investigate the impact of the diffusional mass transfer resistances on adsorption rate of phenols on activated carbon rice husk. To reach this goal batch mechanical agitated vessel is used. Such system insures that concentration of the adsorbate and concentration of adsorbent particles within the agitated vessel is assumed to be uniform throughout. The mass transfer resistances will be followed up by using three models: external mass transfer model, intraparticle diffusion model, and two resistances model. Different equations based on mass transfer coefficient as function of concentration using the three models, were also assessed to find the controlling adsorption step. This study can be used to guide the future analysis to a more understand for the adsorption mechanism of phenol onto activated carbon rice husk.

## 1. Experimental

### 2.1. Adsorbent

Rice husk was obtained from rice mills of El Mansoura city, Egypt. It was used as a precursor for the preparation of activated carbon. The rice husk was washed with distilled water to remove dirt and then dried at room temperature. A tube furnace reactor of 4 cm inner diameter stainless steel pipe was used for the preparation of activated carbon. This reactor was introduced into a calibrated tubular electric furnace open from both sides. A two-stage procedure was followed for the preparation. In the first stage (the carbonization stage) 25 g of rice husk was heated gradually at a temperature rate (50 °C / 15 min) in the tube furnace to 500 °C in a limited amount of air. In the second stage (the activation stage) the temperature of the furnace was raised to 850 °C and hold for 1 hour and carbon dioxide was supplied from a gas cylinder at a constant flow rate. The product was cooled and the yield was calculated.

The infrared spectrum of the prepared carbon was recorded on a Perkin – Elmer FTIR – 1600 series infrared spectrum as KBr discs.

### 2.2. Adsorbate

Three phenolic compounds were used namely: phenol, 2,4- dichlorophenol, and 2,4-dinitrophenol. These compounds were A. R. grade, supplied from BDH.

Stock solutions for each adsorbate was prepared by dissolving the adsorbate in distilled water. The concentration of phenol and its derivatives in the aqueous solutions was determined using spectrophotometer (Shimadzu Model 1601). All the measurements were made at the wavelength that corresponds to maximum absorbance,  $\lambda_{max}$  (270 nm., 285.4 nm and 360 nm for phenol, 2,4 dichlorophenol and 2,4 dinitrophenol, respectively).

### 2.3. Equilibrium study

In the initial laboratory work, experiments were performed to evaluate the relative amenability of the three phenolic pollutants. In this concern, 5ml aliquots of the stock solutions of each concentration were contacted with 2 g of ACRH case of phenol and 2,4- dichlorophenol and 5 g in case of 2,4-dinitrophenol in glass bottles provided with a plastic screw cap. The bottles were shaken using a thermostatic shaker (Kottermann D-1362 Uetze Hanigsen-Germany) for 48 hours in case of phenol and 72 hours for its derivatives to achieve equilibrium concentration. Each mixture was filtered throughout 0.45  $\mu$ m filter paper and the samples were analyzed. All experiments were performed at room temperature (25 $\pm$ 2 °C). The difference between the

initial concentration ( $C_0$ ) and the equilibrium concentration ( $C_e$ ) was calculated to determine the adsorptive capacity ( $q_e$ ) as follow:  $q_e = V (C_0 - C_e)/m$ , where  $V$  and  $m$  are the volume of solution in L and mass of adsorbent in g, respectively.

#### 2.4. Kinetic experiments

A batch adsorber vessel with a standard tank configuration was used in all the experiments. This adsorber initially contained 1.7 dm<sup>3</sup> of the well-stirred aqueous solution of the phenolic compound under study at a known initial concentration. Then a prepared quantity of ACRH with a uniform particle size was introduced into the vessel and the resulting mixture agitated by means of a four-bladed turbine-type mixer. Samples were withdrawn from the system at selected time intervals and analyzed. The process is continued until equilibrium attained in the system. During this process, the temperature of the system was maintained at a constant value (20 + 2°C).

### 3. Results and Discussion

Mass transfer in a porous material has significant effect on the transport process. During adsorption using activated carbon, the adsorbent molecules undergo a tortuous route because of the porous structure. The overall mass transfer performance is subjected to both external resistance and to intraparticle resistance. The mass transfer behavior of the present batch agitated vessel is based on the following differential mass balance with respect to the phenolic molecules to be removed

$$-v \frac{dc}{dt} = kAc \quad (1)$$

Which upon integration using the following initial and boundary conditions respectively:

$$\text{at } t=0, \quad c=c_0$$

$$\text{and, at } t=t, \quad c_t=c$$

$$\ln(c_0/c) = k A t / v \quad (2)$$

where  $c_0$  and  $c$ , are the initial and the final concentrations of phenolic compounds at any time  $t$  (ppm),  $v$  is solution volume (cm<sup>3</sup>),  $t$ : is time (s) and  $A$  is the surface area of activated carbon rice husk (ACRH) (cm<sup>2</sup>).  $A$  was calculated based on the following equation:

$$A=6(m)/(d_p \rho) \quad (3)$$

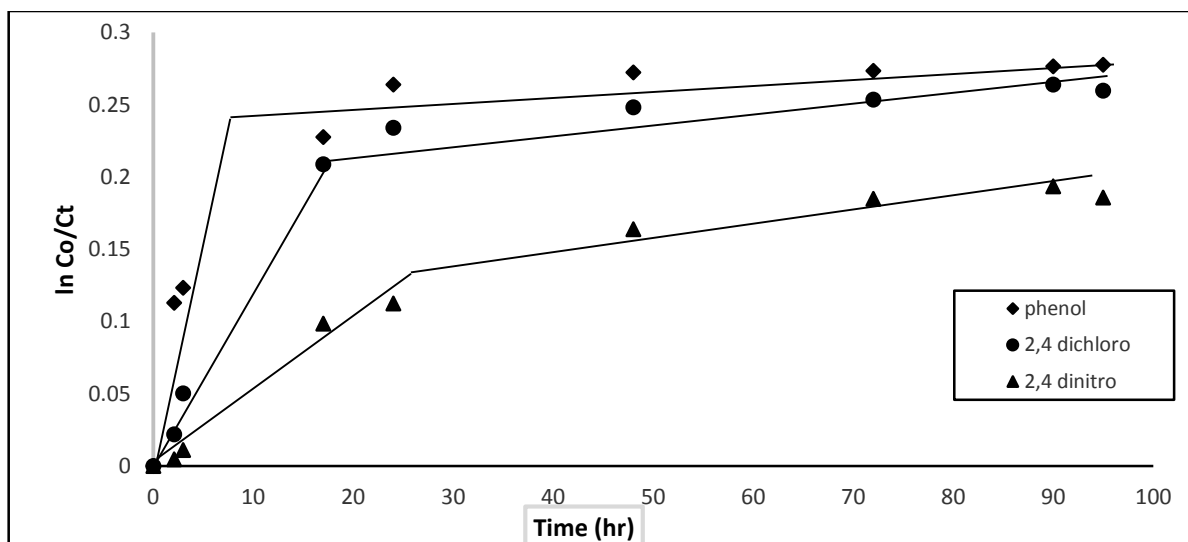
Where  $m$ ,  $\rho$  and  $d_p$  are mass(g), density (g/cm<sup>3</sup>) and particle size (cm) of ACRH respectively. Fig.1 depicted a plot of  $\ln c_0/c$  versus time for the different phenolic components concentrations. It is clear that each curve is divided into two lines indicating that adsorption of phenolic components followed different reaction regimes. An initial rapid rate regime up to 20 h and slower rate regime from 20 to 90 h. This phenomena may be attributed to; at beginning adsorption of phenol is high due to the large number of active sites on ACRH surface lead to high driving force for the external mass transfer

.Consequently, the only resistance for adsorption of phenol is the liquid film diffusion layer surrounding the ACRH surface. On increasing adsorption time, the number of active sites decreased and the driving force decreased and the intraparticle diffusion will be dominated.

Results in Table 1, depicted that phenol has the highest mass transfer coefficient, the next is chlorophenol finally nitrophenol. This is attributed to, not only the lower molecular weight of phenol but also the lower cross sectional area ( $A_m$ ) and the lower effective molecular ( $\sigma_m$ ) diameter. According to Caturla et al [12], the adsorption capacity is lower for an adsorbate with larger molecular volume, therefore phenol was subjected to further mass transfer resistance studies.

The kinetics of mass transfer process can be controlled by reaction kinetics or by one or more diffusion processes (external diffusion or pore diffusion or both). In this study high agitation speed (200 rpm) was used for the kinetic and mass transfer studies. At this high agitation speed the thickness of the boundary layer surrounding the ACRH particles should be minimal. Consequently, the boundary layer resistance or film diffusion should not be major rate controlling factor.

Generally, the adsorption of phenolic compounds on ACRH started by mass transfer of phenolic compounds from the bulk solution to the surface of ACRH particles (external mass transfer) then adsorption onto active sites and finally internal diffusion via pore diffusion (intraparticle diffusion). Adsorption on active sites is rapid [13] thus not considered in any kinetic study in this work. Therefore, the two rate limiting steps considered are: external mass transfer and intraparticle diffusion. The development of models based on the simultaneous occurrence of two such mass transfer steps is quite complex and hence simplifying assumptions have been made in our attempt to describe the adsorption of phenolic compounds on ACRH. The studies of mass transfer resistances will be concentrated on phenol due to its high mass transfer coefficient.



The surface mass transfer coefficient( $k$ ) was calculated from the slope ( $kA/V$ ) of the first part and the  $k$  values are given in Table 1.

Table 1. Mass transfer coefficient, molecular weight, molar volume surface area and molar diameter for phenolic compounds

Compounds	$k$ , cm/s	Mol.(*) Weight	Molar (*) volume mm <sup>3</sup> /mol	A(*) nm <sup>2</sup>	$\sigma_m$ (*) nm
Phenol	0.135	94.1	0.162	0.437	0.746
2,4dichlorophenol	0.061	163	0.199	0.549	0.828
2,4 dinitrophenol	0.084	184.1	0.221	0.597	0.872

(\*) Caturla et.al [12]

### 3.1. External mass transfer

The external mass transfer resistance occurs mainly in the boundary layer film surrounding the ACRH particles and can be described by two resistances. The first resistance is due to convection and diffusion between ACRH particles i.e. from solution bulk to the particles surface. The second resistance is surface adsorption. Consequently, the adsorption rate is rapid until the external surface of ACRH particles are covered by phenol. The model used for determining the external mass transfer coefficient ( $K_f$ ) can be constructed using the boundary conditions given in the following equation

$$K_f = V/A_p [d(c_t/c_o)/dt]_{t=0} \quad (4)$$

Where  $A_p$  is the total surfaces area of ACRH in cm<sup>2</sup> (equation 3).

The influence of initial concentration of phenol is shown in fig.2. Results revealed that at high phenol concentrations the linear section of the curves are close together with the fractional adsorption being low. In contrary at low initial phenol concentration the initial up-take was high.

$K_f$  was determined from the slope of the first linear part ( for the first minute in the process as  $t$  approach 0 ). Fig. 3 shows a plotting of  $\log K_f$  versus  $\log c_o$ , a linear relationship was obtained. The experimental data fit the following equation quite well with a high correlation ( $R^2=0.9990$ )

$$K_f \propto c_o^{0.173} \quad (5)$$

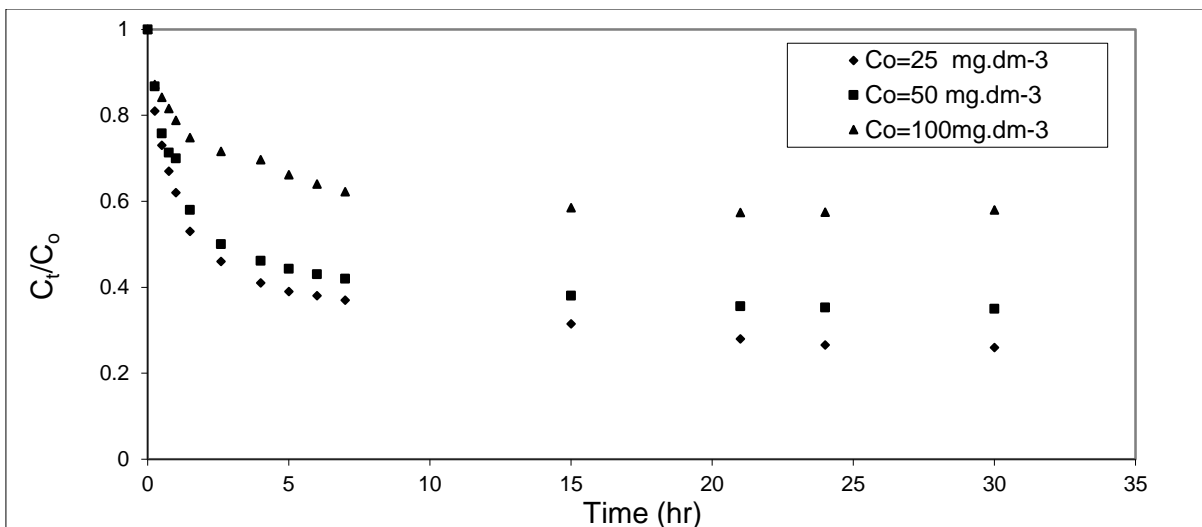


Fig.2. Plot of  $C_t/C_0$  vs time at different phenol concentration (mass of AC is 2.5 g)

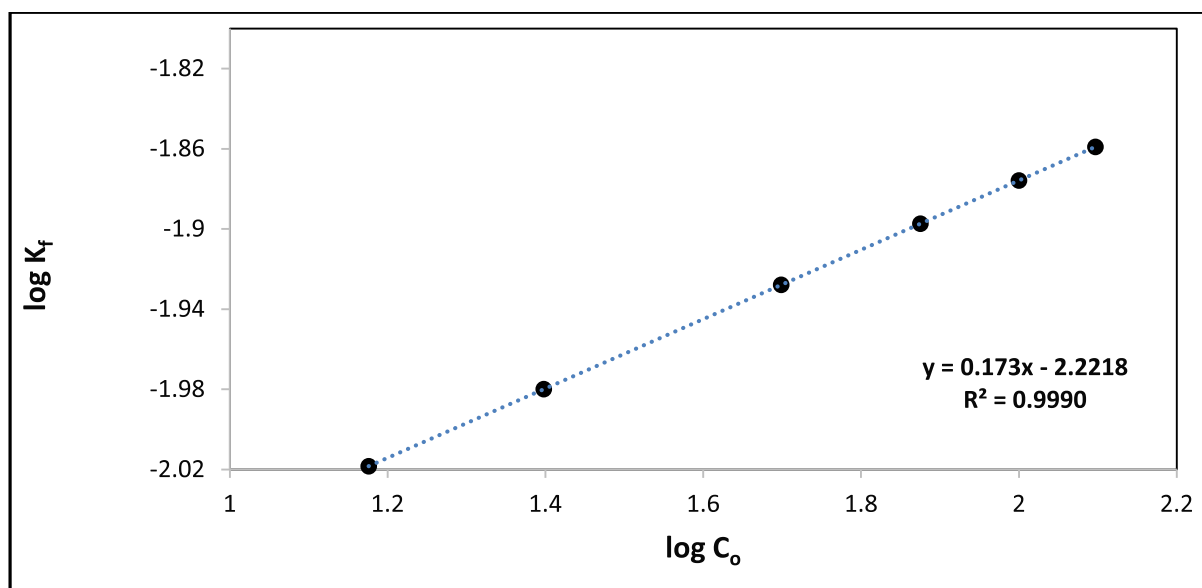


Fig.3. Plot of  $\log K_f$  vs.  $\log c_0$  for external mass transfer adsorption of phenol on ACRH.

### 3.2. Intraparticle diffusion model

In order to evaluate this model, it is assumed that the intraparticle diffusion is the only rate controlling step. The intraparticle diffusion resistance is described by two resistances. The first one is intraparticle diffusion and the second is intraparticle adsorption.

In the present work the model proposed by Weber and Morris [14] (equation 6) was studied, they considered that the intraparticle diffusion step as a single rate controlling.

$$q = K_p t^{0.5} \quad (6)$$

This equation shows the effect of intraparticle diffusion of phenol on ACRH which can be assessed from the plots of  $q_t$  versus  $t^{0.5}$  (Fig. 4) for different phenol concentrations. Figure 4 exhibit three different regions according to Weber and Morris [14] and Nassar [15] and [16]. The first (not shown) is a curved line from origin and the second is straight line represents the intraparticle adsorption rate while the last curve is a plateau where equilibrium is attained when ACRH is saturated with phenol.

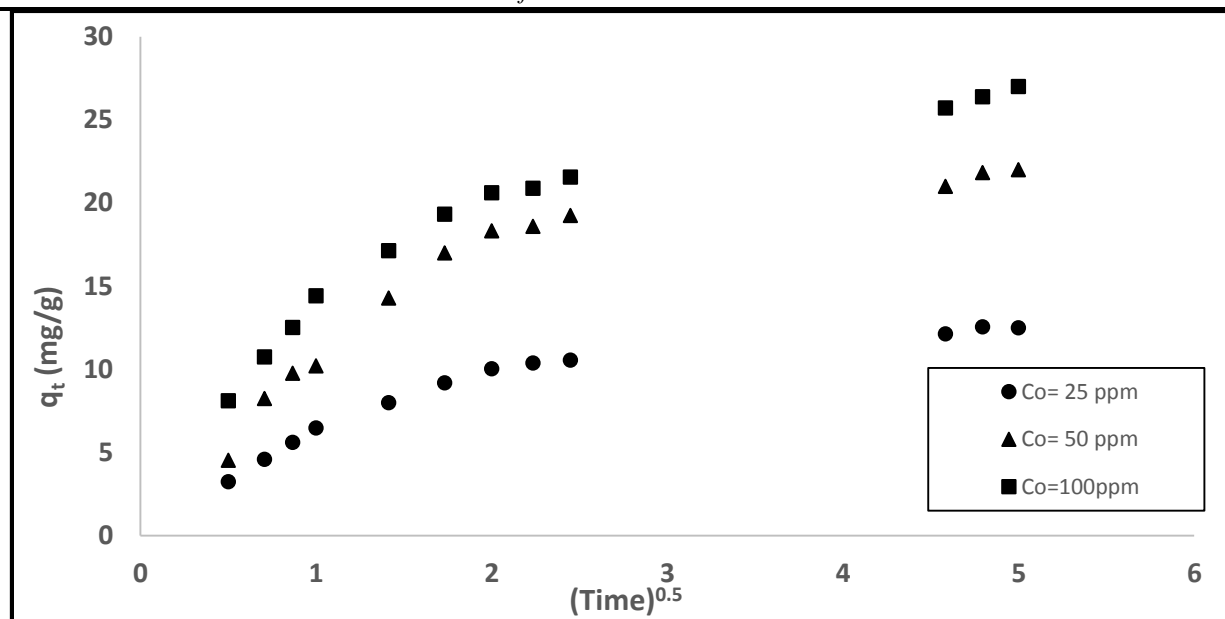


Fig.4. Plot of  $q_t$  versus  $t^{0.5}$  for different initial phenol concentration.

The adsorption rate of intraparticle diffusion ( $K_p$ ,  $\text{mg/g h}^{0.5}$ ) was calculated from the slope of the linear portion (Fig.4). The relationship between  $\log K_p$  versus  $\log c_0$  (Fig.5) is linear, which means according to Findon, et.al [13] is rate controlling step. The obtained data fit the following equation quite well with high correlation ( $R=0.9991$ )

$$\log K_p \propto c_0^{0.478} \quad (7)$$

Comparison equations 5 and 7 indicates that adsorption of phenol in the intraparticle mode is higher than adsorption on external surface of ACRH,

based on  $c_0$  exponents, the intraparticle diffusion is 180% higher than that of the external surface. This finding is in agreement with the work of Souza et.al [17] where they found that the intraparticle diffusion is 93% compared to surface diffusion.

Previous studies by Findon et.al [13] indicated that the single resistance model (external surface and intraparticle diffusion) could not adequately describe the whole adsorption process, therefore in this study two resistance model was carried out.

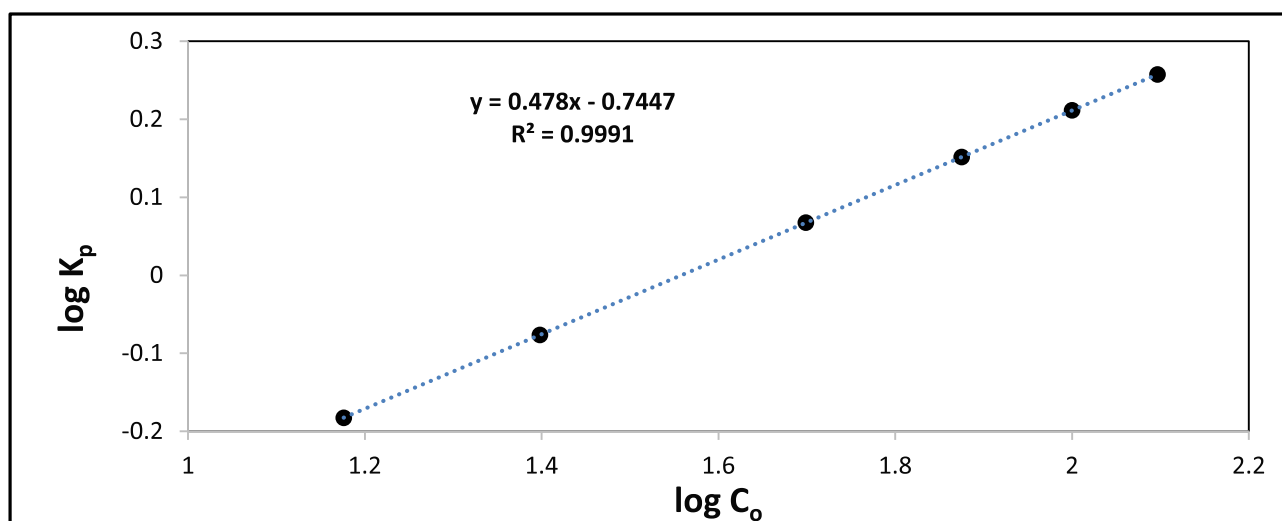


Fig.5. Plot  $\log K_p$  versus  $\log C_0$  for intraparticle diffusion of phenol on ACRH.

### 3.3. Twin -resistance mass-transfer model

The twin mass transfer resistance model is an external mass transfer resistance combined with the pore diffusion resistance models. The pore diffusion model has been used to predict the theoretical concentration/time curve. It is developed to simulate the behavior of a batch adsorber such as used in this study. Provensher and Vogel [18] used this model for solving the corresponding rate relationship with the exponential curve technique, where the experimental and theoretical data are compared in the form of Sherwood number (Sh). In this model the experimental Sherwood number  $Sh_{exp}$  is calculated using the following experimental adsorption rate equation:

$$Sh_{exp} = (R \rho_p K_{PT} q_e) / D_{eff} C_o \quad (8)$$

The theoretical Sherwood number was obtained from the following equation:

$$Sh_{theo} = (1 - C_h \eta) / [(1 - \eta)^{0.67} - (1 - B_i)(1 - \eta)] \quad (9)$$

by comparing values  $Sh_{exp}$  and  $Sh_{theo}$ , it is possible to get values of the mass transfer parameters; liquid phase mass transfer coefficient  $K_f$  and the effective diffusion coefficient ( $D_{eff}$ ) for the phenol/ ACRH system.

The following equation is used to find the agreement between experimental and theoretical values through calculating the experimental and theoretical Sherwood number:

$$(R') = \frac{1}{2} \sum_{i=1}^n [ (Sh^*_{exp} - Sh^*_{theor})_{i=1} / Sh^*_{exp} ] + [ (Sh^*_{exp} - Sh^*_{theor})_{i=n} / Sh^*_{exp} ] \quad (10)$$

Where  $R'$  is the residual  $i$  corresponding to the experimental points and  $n$  is the number of experimental points.  $K_f$  was originally evaluated using initial system conditions in equation (8), then a wide range around this original value was fed to the program to give it flexibility [19] and [20]. In this study,  $K_f$  values was found to be

$$K_T = 79.75 \pm 1.7 \% \text{ cms}^{-1} \quad (11)$$

Similarly, a single effective pore diffusion coefficient ( $D_{eff}$ ) is sufficient to describe all the experimental range. ( $D_{eff}$ ) values found as

$$(D_{eff}) = 0.1 * 10^{-4} \quad (12)$$

Fig.6 shows the relationship of  $K_T$  versus  $C_o$ . The linear relationship was found to fit the following equation:  $K_T = C_o^{0.152}$

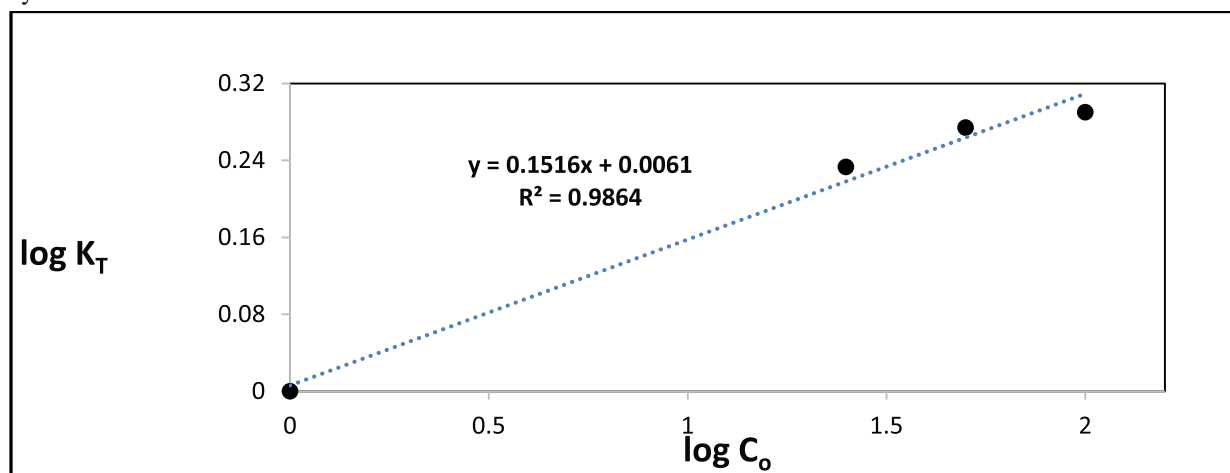


Fig.6. Plot  $\log K_T$  versus  $\log C_o$  for for different phenol concentrations.

On comparing  $K_E$ ,  $K_p$  and  $K_T$  (external mass transfer, intraparticle diffusion and twin resistance mass transfer used equations 5, 7&11) respectively, based on initial concentration of phenol ( $C_o$ ). It can be noticed that  $K_T$  value is close to  $K_f$  value and both are lower than  $K_p$  value. This phenomenon may be

attributed to the fact that adsorption of phenol on ACRH takes place through two mechanisms:

a) At the beginning where the active sites are numerous, the only resistance to the rate of adsorption is the liquid film diffusion layer

surrounding each ACRH particles (external mass transfer model).

b) With increase time the driving force ( $\Delta c$ ) for external mass transfer begin to decrease, and the number of available active sites on ACRH surface becomes less, consequently the intraparticle diffusion become increasingly important. This mechanism is also in accordance with Souza, 2019 where he stated that 93% of adsorption is due to intraparticle diffusion.

The presence of intraparticle mass transfer resistance parameter in the twin resistance mass transfer resistance model, lower the overall mass transfer

Table 2. Properties of activated carbon rice husk

Apparent density g.cm <sup>-3</sup>	Packed density g.cm <sup>-3</sup>	pH	BET surface area m <sup>2</sup> .g <sup>-1</sup>	C%	H%	N%	Ash%
0.136	0.3	10.57	394	41.6	3.8	2.1	52.5

The ACRH is characterized with high C and high ash. Analysis of ash is as follows: 94% silica, 0.25% CaO, 0.23% MgO, 0.78% Na<sub>2</sub>O and 1.1 % K<sub>2</sub>O. Consequently, according to Jang, et al (20 20), ARCH is a suitable adsorbent for adsorption of phenolic compounds due to the presence of high carbon and high silica.

Shen [21] found that, as the carbonization progresses the biomass- thermochemical conversion takes place

process. In the present work the high agitation speed was applied and according to Findon et.al [13] agitation influence only the external mass transfer with no effect on the intraparticle mass transfer step. This finding, confirm the previous assumption that intraparticle diffusion is the controlling step.

### 3.4. Adsorption Isotherms

Different isotherm equations are given in literature for adsorption of phenolic compounds on activated carbon, three of which are used in this study: Langmuir, Freundlich and Dubinin - Rodush (D-R) models. The adsorbent used is ACRH has the following properties Table 2

leading to the increase of aromatic carbon content of the structure. The assumption for the suitability of ACRH in adsorption of phenolic compounds is further supported by Jaing et al. [22], they stated that phenol adsorption was favored by carbon-based adsorbent with aromatic rings and functional groups as carbonyl. The FTIR analysis of the used ACRH is shown in Fig. 7, where C=O is appeared at absorbance band of 2350 cm<sup>-1</sup>

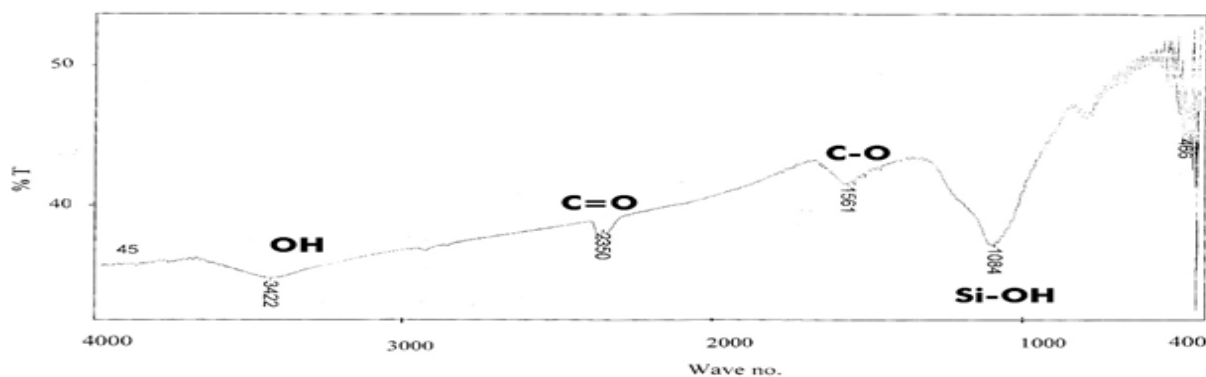


Fig.7. FTIR for the prepared activated carbon

### Langmuir model

The model is based on the assumption that all sites possess equal affinity for the adsorbate. The adsorption takes place on the adsorbent surface forming mono layer. The linear form the Langmuir model is as follows:

$$1/q_m = 1/q_m + C_e(k_L/q_m) \quad (13)$$

The linear fitting results of adsorption using Langmuir isotherm is predicted in Fig.8 and the parameters from the fitting data are introduced in Table3.



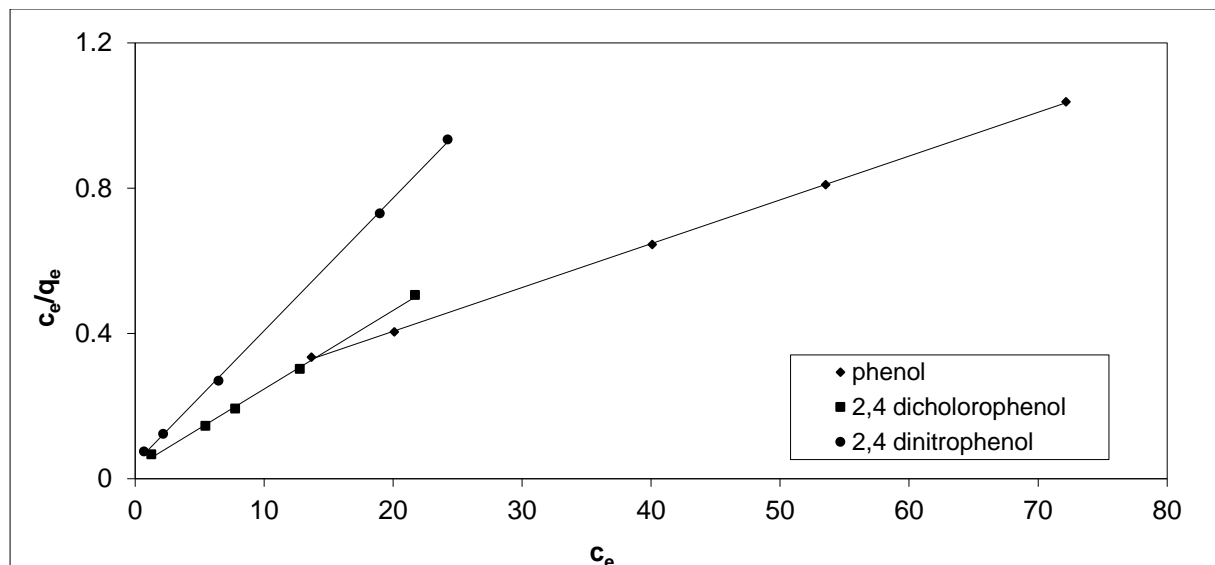


Fig. 8. Langmuir isotherm for phenol and its derivatives onto activated carbon.

The very high values of  $R^2$  for the three phenols suggested that adsorption of phenol on ACRH follows Langmuir model implying monolayer adsorption. Moreover, the values of  $R_L$  [ $R_L = 1/(1+k_L C_0)$ ] for the three adsorption systems are in the range 0-1 confirming the favorability of the adsorption [15]. The results in table 3 indicate that the values of  $q_m$  (maximum adsorption) have a descending order:

Phenol > 2,4 dichlorophenol > 2, 4 dinitrophenol

Based on Langmuir parameters (table 3), the following equations represent the adsorption of phenolic compounds on ACRH

For, phenol:  $1/q_e = 0.0069 + C_e/(4.8 \times 10^{-5})$

For 2,4 dichlorophenol:

$1/q_e = 0.012 + C_e/(1.65 \times 10^{-2})$

For 2,4 dinitrophenol:  $1/q_e = 0.034 + C_e/(0.034)$

These equations can be used in design of batch adsorber for removal of phenols using ACRH adsorbent

#### Freundlich model

The model is based on the equilibrium relationship between heterogeneous surfaces. The model assumes that the adsorption sites are distributed exponentially with respect to the heat of adsorption and it is used to describe the heterogeneous surface energy. The logarithmic linear form can be presented as follows:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln c_0 \quad (14)$$

The Freundlich isotherm is depicted in Fig. 9, and the parameters obtained from the fitting of the experimental data to the model, are presented in Table 3. The correlation coefficients from the linear regression ( $R^2$ ) are less than that of Langmuir model, suggesting that adsorption of phenols on ACRH fits

Table 3. Linear adsorption parameters for Langmuir, Freundlich and D-R. models

Isotherms Compounds	Langmuir				Freundlich			D-R. model	
	$q_m$	$k_L$	$R_L$	$R^2$	$n$	$k_F$	$R^2$	$E$	$R^2$
Phenol	145	0.007	0.12	0.978	3.14	18.5	0.98	9.1	0.982
2,4dichlorophenol	85	0.14	0.014	0.964	3.13	19.5	0.89	11.2	0.882
2,4dinitrophenol	29	0.64	0.023	0.998	3.65	12.2	0.87	15.8	0.899

Langmuir model. However, values of the Freundlich parameter(n) are greater than 1 for the three phenols

confirming the favorability of adsorption [15].

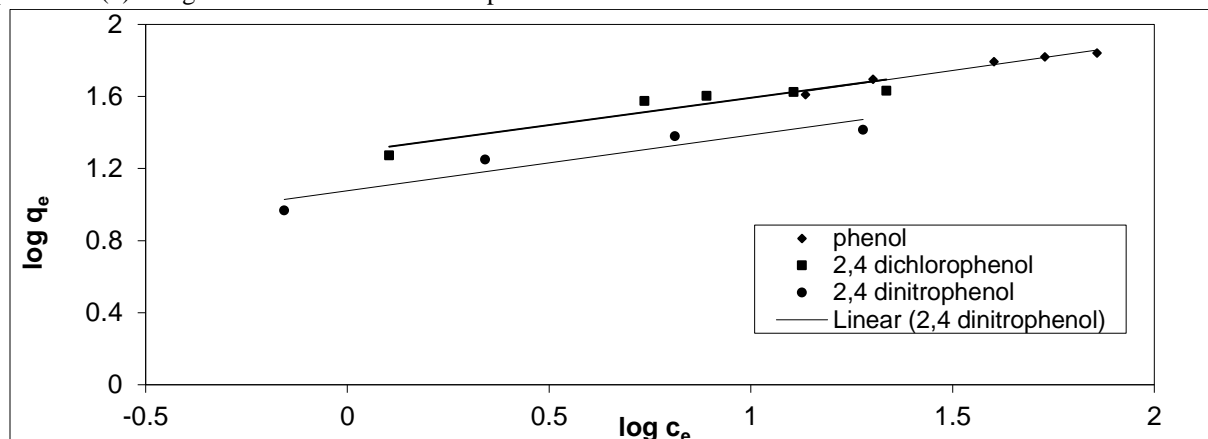


Fig.9. Freundlich isotherm for phenol and its derivatives onto activated carbon

Based on Freundlich parameters (table3) the following equations represent the adsorption of phenols on ACRH:

$$\text{Phenol:} \quad \ln q_e = 2.92 + 0.318 (\ln c_e)$$

$$\text{2-4 dichlorophenol:} \quad \ln q_e = 2.95 + 0.302 (\ln c_e)$$

$$\text{2-4 dinitrophenol:} \quad \ln q_e = 2.5 + 0.082 (\ln c_e)$$

*Duhinin –Rodush (D.R) isotherm*

The linear form of D-R model is as follows:

$$\ln q_e = \ln q_m - BE^2 \quad (15)$$

$$\text{Where } E = RT \ln \left(1 + \frac{1}{c_e}\right)$$

B is constant related to the mean free energy of adsorption, E (kJ/mol<sup>-1</sup>) is calculated by using the following equation

$$E = 1/\sqrt{2B}$$

The E parameter helps to identify, if adsorption has physical or chemical nature. According to Bhakta et.al [23] if  $E > 16$  kJ/mol<sup>-1</sup> the adsorption process is chemical, if  $8 < E < 16$  kJ/mol<sup>-1</sup> the adsorption process is ion exchange, and if  $E < 8$  kJ mol<sup>-1</sup> the adsorption is physical.

Values of E for adsorption of the phenolic compounds lies between 9.1 to 15.8 kJ mol<sup>-1</sup>, which pointed out that adsorption of phenols is ion exchange. This finding is not in agreement with Shen [21] since he assumed that adsorption of phenols on ACRH is of chemisorption nature (no evidence was given). The discrepancy is due to the way of preparation of ACRH where Shen used steam at 900 °c in the first stage and KOH for the second stage, while in the present work, in the first stage limited air

was used at 500 °c, then CO<sub>2</sub> was used in the second stage.

#### 4. Conclusions

Based upon the experimental results in this study, the following conclusions can be drawn:

- 1-The adsorption behavior and mechanism were illustrated by the mass transfer diffusional resistance models as well as adsorption isotherms.
- 2- Adsorption capacity of phenol on activated carbon rice husk is higher (attributed to the lower molecular volume) than the chlorophenol and nitrophenol has the lowest adsorption capacity (attributed to the higher molecular volume).
- 3- The relationship of mass transfer coefficient, versus time shows two adsorption regimes, the first one is due to adsorption on the external surfaces while the second regime is due to intraparticle adsorption.
- 4- Adsorption of phenol based on the intraparticle model. is 180 % higher than the adsorption on external surface of ACRH, which is attributed to the larger surface area of the pore structure.
- 5- The value of mass transfer coefficient based on the twin resistance model is close to that of external mass transfer model and both are lower than that of intraparticle diffusion model. This is due to the following:

In case of intraparticle model (as a single resistance) the entrance to the pore structure is free for diffusion of phenol, while in case of external surface and twin

resistance models, the entrance of pores may be blocked with the adsorbent.

### 5. Nomenclature

A: Area in Equation 3

$A_p$ : External surface area of ACRH particle ( $\text{cm}^2$ )

$A_m$ : Particle cross-sectional area ( $\text{m}^2$ )

B: D-R model constant

$B_i$ : Biot number ( $=k_f R/D_{\text{eff}}$ )

$C, C_0$ : Initial liquid phase concentration ( $\text{mg dm}^{-3}$ )

$C_e$ : Equilibrium liquid-phase Concentration ( $\text{mg dm}^{-3}$ )

$C_t$ : Liquid-phase concentration after time  $t$ , ( $\text{mg dm}^{-3}$ )

$D_{\text{eff}}$ : Effective pore diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )

$d_p$ : Mean particle diameter (mm)

E: Mean free energy ( $\text{kJmol}^{-1}$ )

$k$ : mass transfer coefficient ( $\text{Cm s}^{-1}$ )

$K_{\text{ad}}$ : Equilibrium rate constant ( $\text{h}^{-1}$ )

$K_f$ : External mass coefficient transfer ( $\text{cm s}^{-1}$ )

$k_F$ : Freundlich constant

$k_L$ : Langmuir constant

$K_T$ : Twin resistance mass transfer Coefficient ( $\text{cm s}^{-1}$ )

$K_p$ : Intra particle diffusion rate constant ( $\text{mg/g h}^{0.5}$ )

$m$ : adsorbent mass (g)

$q_e$ : Equilibrium solid-phase concentration ( $\text{mg g}^{-1}$ )

$R$ : Residual of Sherwood number

$Sh_{\text{exp}}$ : Modified experimental Sherwood number

$Sh_{\text{theor}}$ : Modified theoretical Sherwood number

$t$ : Time (s/min/h)

$V$ : Volume of liquid in reactor ( $\text{dm}^3$ )

$\eta$ : Dimensionless solid-phase concentration

$\rho_p$ : Particle density ( $\text{g cm}^{-3}$ )

$\sigma_m$ : Effective molecular diameter (nm)

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