

KINETIC STUDIES OF COLOUR AND PHENOL REMOVAL FROM WASTEWATER USING MANGO SEED SHELL ACTIVATED CARBON

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ABSTRACT

Kinetic studies by batch technique were carried out using activated carbon prepared from mango seed shell for the adsorption of colour and phenol from wastewater. The data generated from the studies were used for kinetic modelling in order to determine the rate and mechanism of adsorption. The results revealed that adsorption was best fitted by the pseudo-second order model for both methylene blue (MB) and phenol adsorptions. Intra-particle diffusion kinetic plots did not pass through the origin, indicating that intra-particle diffusion was not the only rate controlling mechanism. The results showed that mango seed shell activated carbon (MSSAC) is more effective for adsorption of colour than phenol in wastewater.

KEYWORDS: Kinetics, Adsorption, Mango seed shell, Colour, Phenol, Wastewater

INTRODUCTION

Adsorption is a time-dependent process and it is very important to know the rate of adsorption for design purposes. The rate and mechanism of adsorption is controlled by various factors like physical and/or chemical properties of adsorbent, ambient temperature, pH of medium and nature of adsorbate. The prediction of adsorption rate gives important information for designing adsorption systems. Kinetic models have been used to investigate the mechanism and the rate controlling steps of sorption which are helpful for selecting optimum operating conditions for the full-scale batch process.

Pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion kinetic models have been used by various investigators. Among these are adsorption of basic red by *Euphorbia Antiquorum L* wood based activated carbon (Sivakumar and Palanisamy, 2009), removal of Cu(II) ion from aqueous solution using sago

waste as adsorbent (Maheswari *et al*, 2008); phenol removal from aqueous systems by tendu leaf refuse (Nagda *et al*, 2007); adsorption of phenol and dye from aqueous solution using chemically modified date pits activated carbons (Belhachemi and others, 2009) and adsorption of remazol black 5 on palm kernel shell activated carbon (Zawani *et al*, 2009). Others are the biosorption of zinc onto *gallus domesticus* shell powder (Kalyani *et al*, 2009), adsorption of methylene blue onto gulmohar plant leaf powder (Ponnusami *et al*, 2009), methylene blue (MB) removal from aqueous solution by adsorption on treated sawdust (Bello *et al*, 2010) among others.

This study is fashioned to determine the kinetics of adsorption of colour and phenol from wastewater using activated carbon prepared from mango seed shells as adsorbent. This will be achieved by calibrating kinetic models proposed in literature in order to understand the mechanism of adsorption of these pollutants by mango seed shell activated carbon (MSSAC).

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This study is of interest because knowledge of adsorption rate and mechanism is very important for selecting optimum operating conditions for design purposes.

THEORETICAL CONSIDERATION

Kinetics of adsorption, describing the solute uptake rate, which in turn governs the contact time of adsorption process, is one of the important characteristics defining the efficiency of adsorption (Patil *et al*, 2006). In order to investigate the mechanism of MB and phenol adsorption by mango seed shell based activated carbon (MSSAC), the following four kinetic models were considered:

Pseudo-First-Order Model

The pseudo-first-order rate expression based on solid capacity is generally expressed as follows (Lagergren, 1898):

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \dots\dots\dots (1)$$

Where, $\frac{dq_t}{dt}$ is the rate of adsorption, q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), q_t is the amount adsorbed at any time t (mg/g), k_1 is the rate constant of first order adsorption (l/minutes). After integration and applying boundary conditions, $t = 0$ to t and $q_t = 0$ to q_t ; Equation (1) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \dots\dots\dots (2)$$

Values of adsorption rate constant (k_1) for the adsorbate are determined from the straight line plot of $\log (q_e - q_t)$ against t . A high value of the correlation coefficient is an indication that the rate of removal of the adsorbate by the adsorbent follows the pseudo-first-order equation.

The parameter $\log (q_e)$ is an adjustable parameter and often it is found not equal to the intercept of a plot of $\log(q_e - q_t)$ against t , whereas in a true first order model, $\log(q_e)$ should be equal to the intercept of a plot of $\log(q_e - q_t)$ against t . Therefore one has to find some means of extrapolating the experimental data to $t = 0$, or treat q_e as an adjustable parameter to be determined by trial and error. For this reason, it is

necessary to use trial and error to obtain the equilibrium sorption capacity, q_e , to analyze the first order model kinetics (Ho and Mckay, 1998).

Pseudo-Second-Order Model

The pseudo-second-order equation is also based on the sorption capacity of the solid phase. It predicts the behaviour over the whole range of data. Furthermore, it is in agreement with chemisorption being the rate controlling step and is expressed as (Ho *et al*, 2000):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \dots\dots\dots (3)$$

Where, k_2 is the rate constant of second order-adsorption (g/mg.min). $\frac{dq_t}{dt}$, q_t , q_e and t are as defined under Equation 1. For the same boundary conditions as in Pseudo-first order model, the integrated form of Equation (3) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \dots\dots\dots (4)$$

If the initial sorption rate, h (mg/ g. minutes) at $t = 0$ is defined as:

$$h = k_2 q_e^2 \dots\dots\dots (5)$$

Then Equations (4) and (5) become:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \dots\dots\dots (6)$$

Equation (6) does not have the disadvantage of the problem with assigning an effective q_e . If pseudo-second order kinetics are applicable, the plot of t/q_t against t of Equation (6) should give a linear relationship from which q_e and h values will be determined from the slope and intercept of the plot respectively and there is no need to know any parameter beforehand (Ho and Mckay, 1998). k_2 will then be determined from Equation (5).

Elovich Model

The Elovich equation is mainly applicable for chemisorption kinetics. The equation is often valid for systems in which the adsorbing surface is heterogeneous (Sivakumar and Palanisamy,

2009). The Elovich model is generally expressed in linear form as:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad \dots\dots\dots (7)$$

Where,

α is the initial adsorption rate (mg/g minutes) and $\hat{\alpha}$ is the desorption constant and is related to the extent of surface coverage and the activation energy for chemisorption (g/mg). q_t , q_e and t are as defined under Equation 1. A plot of q_t against $\ln t$ gives a linear trend with a slope of $(1/\hat{\alpha})$ and an intercept of $1/\hat{\alpha} \ln(\hat{\alpha} \hat{\alpha})$.

Intra-particle Diffusion Study

The most commonly used technique for identifying the mechanism involved in the adsorption process is by using intra-particle diffusion model as proposed by Weber and Morris (Abdelwahab, 2007) thus:

$$q_t = K_d t^{1/2} + I \quad \dots\dots\dots (8)$$

Where, K_d is the intra-particle diffusion rate constant. q_t and t are as defined under Equation 1. If intra-particle diffusion occurs, then a plot of q_t against $t^{1/2}$ will be linear and the line will pass through the origin if intra-particle diffusion was the only rate limiting parameter controlling the process. Otherwise, some other mechanism such as external mass transfer is also involved. Values of I give an idea about the thickness of the boundary layer.

MATERIALS AND METHODS

100ml of test samples of pH 7 with initial methylene blue (MB) concentration of 87 Pt-Co units were measured in 6 different 500ml beakers. Specified adsorbent doses of 200mg were added to each beaker and stirred at 98 revolutions per minute (rpm) using electrically operated paddles of a flocculator (ESF 12/10 model). In the case of phenol, the carbon dose and pH used were respectively 1000mg and 8, while the initial phenol concentration was 0.047mg/l. kinetic studies were performed at a constant room temperature of $34 \pm 2^\circ\text{C}$. The preparation procedure and the characteristics of the mango seed shell activated carbon (MSSAC) are reported elsewhere (Akpen, 2011; Akpen et al, 2011).

Samples were taken at preset time intervals of 5, 10, 20, 30, 40, 50, 60, 90 and 120 minutes and 30, 60, 90, 120, 150 and 180 minutes in the case of MB and phenol respectively. The contents were allowed to settle for 2 minutes and filtered through no. 42 filter paper prior to analysis in order to minimize interference of the carbon fines with the analysis. The residual concentrations of MB and phenol were analysed according to standard methods as specified in HACH Model DR/2000 Spectrophotometer operator's manual. The carbon particle size used was 150-850 μm in the case of MB and 150-425 μm for phenol. The same procedures were repeated for other initial concentrations of 126, 181, 240 and 262 Pt-Co units in the case of MB and 0.069, 0.074, 0.114 and 0.123mg/l in the case of phenol.

The amount of adsorption at time t , q_t , was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad \dots\dots\dots (9)$$

Where, C_0 and C_t are the liquid-phase concentration of pollutants at initial and any time t , respectively. V is the volume of the solution, and m is the mass of dry adsorbent used.

RESULTS AND DISCUSSION

The data on kinetics of adsorption was processed to understand the dynamics of adsorption process in terms of the order of rate constant. A typical pseudo first-order plot for the adsorption of MB by MSSAC is given in Fig.1. The calculated rate constants and q_e values and the corresponding linear regression correlation coefficients, r values for all the kinetic models are presented in Tables1-4. It is obvious from Tables1-4 that, the first-order kinetic model did not fit well to the experimental data because the experimental and calculated values of the equilibrium removal capacity, q_e were different even though the correlation coefficients were high (0.829-0.990). The pseudo first-order rate constant k_1 generally decreased with increase in initial MB concentration for all the experimental carbons except *Dausha* 1:2 adsorbent. For *local* 1:2 adsorbent, k_1 decreased from 0.154 to 0.039 min^{-1} when the initial MB concentration was increased from 87-262 Pt-Co units.

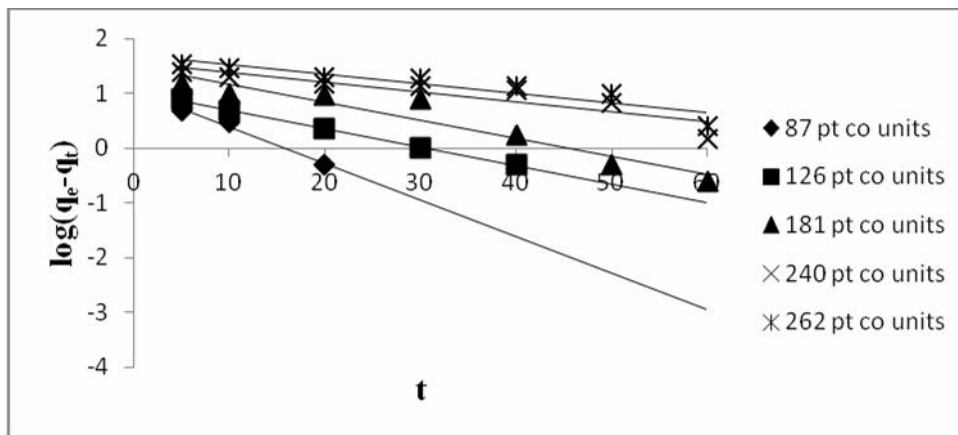


Fig. 1: Pseudo-First-Order Plots of MB Adsorption on *local 1:2*

A typical pseudo first-order plot for the adsorption of phenol by MSSAC is given in Fig.2. The corresponding parameters and coefficients are depicted in Table 5. The correlation coefficients (r) ranged from 0.424 to 0.750. Just as in the case of MB adsorption, first-order kinetic model did not fit well to the experimental data because

the experimental and calculated values of the equilibrium removal capacity, q_e were significantly different. Besides, the low r values suggest that the adsorption data fitted poor to pseudo first-order kinetics. Thus, the adsorption of phenol onto MSSAC does not follow the pseudo first-order rate model.

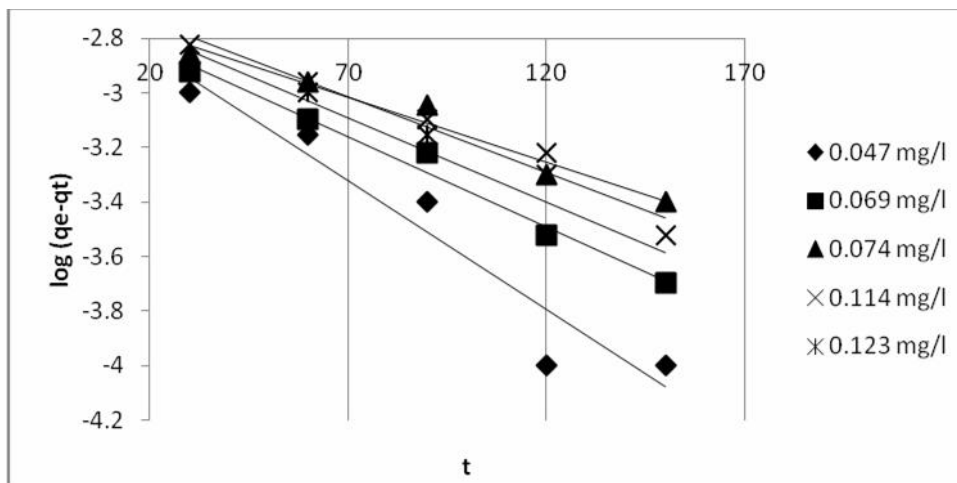


Fig. 2: Pseudo-First-Order Plots of Phenol Adsorption on *local 1:2*

Figs.3 shows a typical pseudo second-order plot for the adsorption of MB by MSSAC at various initial concentrations and the corresponding second order kinetic rate constants and correlation coefficients are given in Tables 1-4. Unlike pseudo first order model, good

correlation is observed between experimental data and the pseudo-second-order kinetic model with r values generally higher than 0.99. For the four variations of the mango seed shell activated carbons (MSSAC) studied, the differences between the experimental and the calculated

values of the equilibrium removal capacity, q_e were not significant. This suggests that the rate-limiting step in these biosorption systems may be chemisorptions involving valence forces through sharing or exchange of electrons between adsorbent and MB as reported by Ho and McKay (1999). The equilibrium sorption capacity, q_e increase with increase in initial MB concentration while initial sorption rate, h generally decreased with increase in initial MB concentration for all the experimental activated carbons studied.

It can be noticed that the pseudo second-order rate constant, k_2 for *Dausha* 1:2 decreased from 0.0412 to 0.000743 (Pt-co units /mg min) with increase in initial MB concentration from 87-262 Pt-co units (see Table 1). The decrease in the rate of MB removal with increasing initial MB concentration may be due to decreasing MB diffusivity as a result of the association of dye molecules to form bulky aggregates which becomes more pronounced at high dye concentration.

Table 1: Adsorption Kinetic Model Rate Constants for *Dausha* 1:2, at different Initial Concentrations of MB

Initial conc.(Pt-Co Units)	Pseudo First Order Model				Pseudo Second Order Model				Elovich Model			Intra-particle Diffusion Model		
	q _e (exp.)	q _e (cal.)	K ₁	r	h	q _e	K ₂	r			r	K _d	r	l
87	14.5	9.86	0.143	0.978	9.174	14.925	0.0412	0.999	263.39	0.634	0.858	0.480	0.723	10.51
126	21.0	9.68	0.032	0.829	2.825	22.727	0.0055	0.997	22.02	0.310	0.959	1.152	0.947	10.13
181	30.17	37.93	0.0714	0.921	2.646	34.48	0.0022	0.993	10.0333	0.141	0.947	2.348	0.865	9.069
240	40.0	54.33	0.069	0.975	2.762	47.62	0.00123	0.993	5.506	0.919	0.973	3.643	0.901	7.401
262	43.67	62.66	0.067	0.980	2.294	55.556	0.000743	0.980	4.789	0.0767	0.963	4.378	0.894	4.581

Table 2: Adsorption Kinetic Model Rate Constants for *Dausha* 1:3 at different Initial Concentrations of MB

Initial conc.(Pt-Co Units)	Pseudo First Order Model				Pseudo Second Order Model				Elovich Model			Intra-particle Diffusion Model		
	q _e (exp.)	q _e (cal.)	K ₁	r	h	q _e	K ₂	r			r	K _d	r	l
87	14.5	10.07	0.053	0.977	2.192	15.625	0.00898	0.998	17.22	0.454	0.961	0.775	0.934	7.299
126	21	19.06	0.044	0.950	2.075	22.73	0.00402	0.992	9.401	0.271	0.987	1.320	0.977	7.923
181	29.67	13.61	0.025	0.977	3.984	31.26	0.00408	0.998	47.35	0.246	0.997	1.442	0.979	14.97
240	37	36.64	0.023	0.990	1.065	50.0	0.00043	0.992	2.63	0.101	0.985	3.636	0.997	-1.633
262	36.67	37.84	0.021	0.979	0.658	71.429	0.0013	0.931	2.023	0.0922	0.974	3.973	0.986	-5.630

Table 3: Adsorption Kinetic Model Rate Constants for *Local* 1:2 at different Initial Concentrations of MB

Initial conc.(Pt-Co Units)	Pseudo First Order Model				Pseudo Second Order Model				Elovich Model			Intra-particle Diffusion Model		
	q _e (exp.)	q _e (cal.)	K ₁	r	h	q _e	K ₂	r			r	K _d	r	l
87	21.75	11.641	0.154	0.990	23.81	22.222	0.048	0.9995	54956.483	0.672	0.880	0.46	0.752	17.92
126	31.75	11.015	0.078	0.998	20.408	32.258	0.020	0.9995	9172.321	0.393	0.935	0.813	0.828	24.52
181	45.25	31.189	0.076	0.956	11.364	47.619	0.005	0.998	376.179	0.193	0.949	1.787	0.903	28.99
240	60	35.975	0.039	0.894	8.13	66.667	0.002	0.997	98.389	0.119	0.971	3.005	0.964	30.68
262	65.5	49.204	0.039	0.925	6.289	76.923	0.001	0.996	26.126	0.083	0.981	4.289	0.967	24

Table 4: Adsorption kinetic model rate constants for *Local* 1:3 at different Initial Concentrations of MB

Initial conc.(Pt-Co Units).	Pseudo First Order Model				Pseudo Second Order Model				Elovich Model			Intra-particle Diffusion Model		
	q _e (exp.)	q _e (cal.)	K ₁	r	h	q _e	K ₂	r			r	K _d	r	l
87	21.75	9.48	0.055	0.986	6.757	22.73	0.013	0.995	258.028	0.416	0.973	0.798	0.893	14.55
126	31.5	8.77	0.023	0.832	6.173	33.33	0.006	0.999	101.342	0.245	0.985	1.41	0.942	18.35
181	45.25	22.336	0.051	0.981	10.526	47.62	0.005	0.995	109.135	0.160	0.965	2.088	0.890	26.48
240	60	35.24	0.041	0.969	8.772	66.67	0.002	0.994	63.601	0.108	0.991	3.207	0.951	29.68
262	65.5	47.97	0.035	0.938	5.78	76.92	0.001	0.995	21.386	0.08	0.984	4.466	0.971	21.99

The correlation coefficients, r ranged from 0.980 to 0.999, which is higher than pseudo first-order values (0.829-0.980). From these results it can be suggested that pseudo second-order describes the adsorption of MB by MSSAC better than pseudo first order model. Similar results

were reported by Sivakumar and Palanisamy (2009) on the adsorption of basic red 29 by euphorbia antiquorum L based activated carbon. The same behaviour was observed by Bello *et al* (2010) for the adsorption of methylene blue onto treated saw dust.

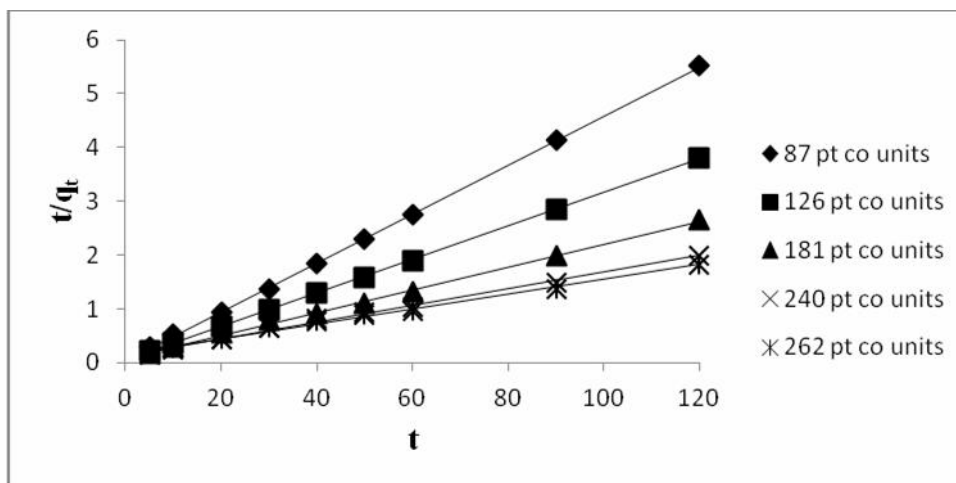


Fig. 3: Pseudo-Second-Order Plots of MB Adsorption on *local* 1:2

In the case of phenol adsorption, a typical second order plot is presented in Fig.4, while the adsorbent parameters and correlation coefficients are shown in Table 5. The high values of the rate

constant k_2 (8.75-18.79) and correlation coefficients, r (0.997-0.999) suggest that the kinetics of phenol adsorption follows the pseudo-second order kinetic model.

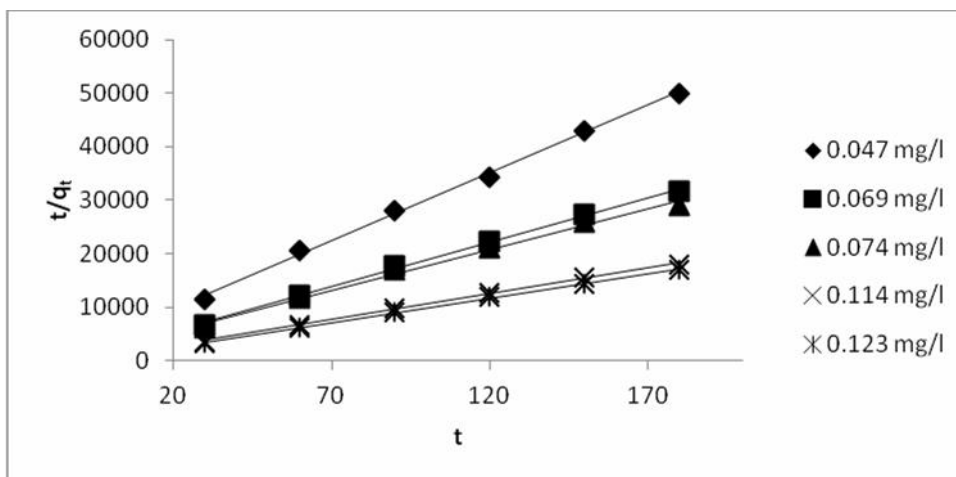


Fig. 4: Pseudo-Second-Order Plots of Phenol Adsorption on *local* 1:2

A typical Elovich plot for the adsorption of MB by MSSAC at various initial dye concentrations is given in Fig.5. The plots are linear with good correlation coefficients ($r = 0.858$ to 0.997). The initial adsorption rate, \hat{a} , increased, while desorption constant, \hat{b} decreased with increase in

initial dye concentration for all the experimental activated carbons (see Tables 1-4). The increase in the values of \hat{a} can be attributed to an increase in the driving force for mass transfer, i.e. more MB molecules are able to reach the surface of the adsorbent in a shorter period of time.

Table 5: Adsorption Kinetic Model Rate Constants for Dausha 1:2, Local 1:2 and Local 1:3 at different Initial Concentrations of Phenol

Adsorbent	Initial Conc. (Mg/l)	Pseudo-First Order Model				Pseudo-Second Order Model			
		q_e (exp.)	q_e (cal.)	K_1	r	h	q_e	K_2	r
<i>Dausha 1:2</i>	0.047	0.0033	9.75×10^{-5}	-0.0253	0.4313	0.000143	0.00375	10.14	0.998
	0.069	0.0052	2.52×10^{-5}	-0.0507	0.750	0.000434	0.00556	14.01	0.999
	0.074	0.0057	8.99×10^{-5}	-0.00364	0.500	0.000502	0.00598	14.03	0.998
	0.114	0.0094	7.36×10^{-5}	-0.0299	0.562	0.00171	0.00953	18.79	0.999
	0.123	0.0101	9.89×10^{-5}	-0.0276	0.508	0.00160	0.01034	14.97	0.999
<i>Local 1:2</i>	0.047	0.0036	7.74×10^{-5}	-0.0253	0.424	0.00021	0.00396	13.37	0.998
	0.069	0.0057	1.02×10^{-4}	-0.0253	0.486	0.000458	0.00603	12.61	0.999
	0.074	0.0067	1.37×10^{-4}	-0.0276	0.527	0.000406	0.00655	9.45	0.996
	0.114	0.0100	1.47×10^{-4}	-0.0253	0.506	0.00111	0.0103	10.37	0.999
	0.123	0.0106	1.23×10^{-4}	-0.0253	0.492	0.00148	0.0109	12.44	0.999
<i>Local 1:3</i>	0.047	0.0035	8.26×10^{-5}	-0.0253	0.458	0.000192	0.00384	13.01	0.999
	0.069	0.0055	1.07×10^{-4}	-0.0253	0.475	0.000399	0.000588	11.56	0.999
	0.074	0.0059	1.44×10^{-4}	-0.0253	0.502	0.000351	0.000633	8.75	0.997
	0.114	0.0096	1.37×10^{-4}	-0.0276	0.526	0.00105	0.00989	10.73	0.998
	0.123	0.0103	1.13×10^{-4}	-0.0276	0.497	0.00149	0.0106	13.33	0.999

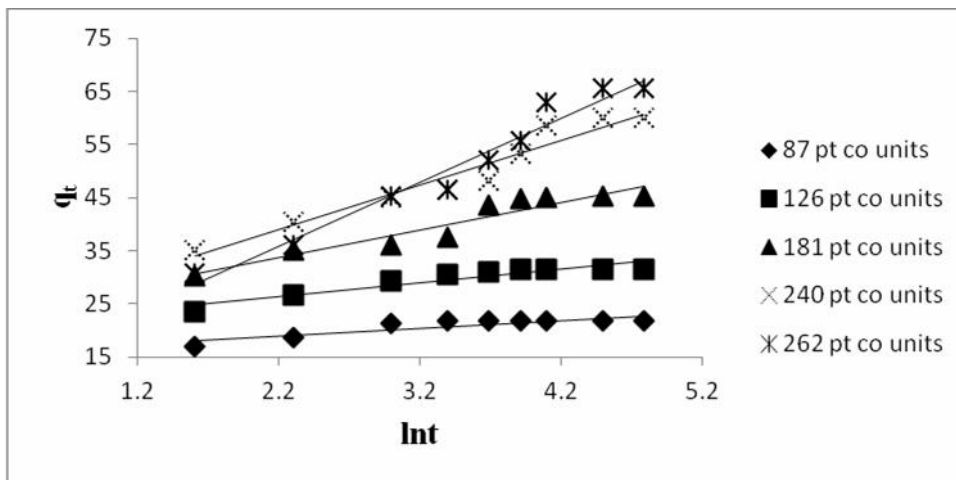


Fig. 5: Elovich Model Plots of MB Adsorption on *local 1:2*

Fig.6 depicts a typical intra-particle kinetic plot for the four experimental carbons with respect to MB adsorption. If intra-particle diffusion occurs, then a plot of q against $t^{1/2}$ will be linear and the line will pass through the origin if the intra-particle diffusion was the only rate limiting parameter controlling the process. However, for this present study, the linear plots for a wide range of contact times do not pass through the origin. This deviation from the origin may be due to the

variation of mass transfer in the initial and final stages of adsorption (Sivakumar and Palanisamy, 2009). This indicates that although intra-particle diffusion was involved in the adsorption process, it was not the sole sorption rate-controlling step. This also confirms that adsorption of MB on the adsorbent was a multi-step process, involving adsorption on the external surface and diffusion into the interior.

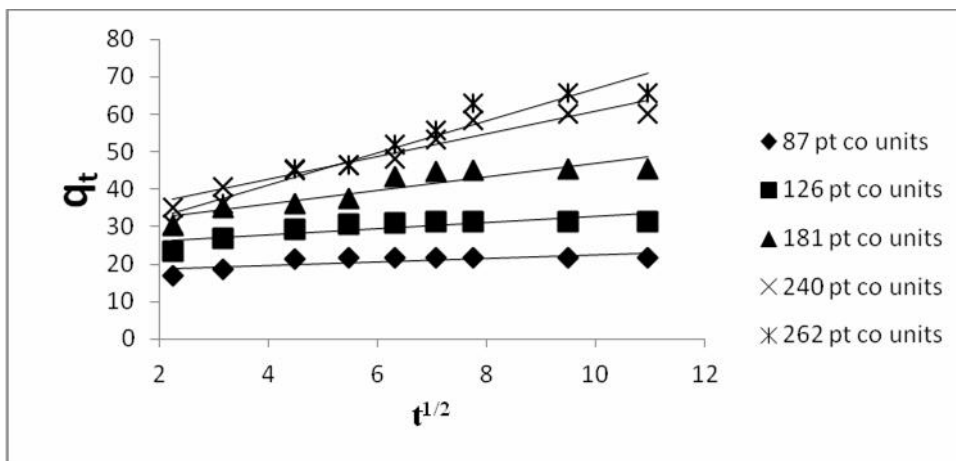


Fig. 6: Intra-particle Diffusion plots of MB adsorption on *Local 1:2*

The intra-particle diffusion rate, k_d and the linear correlation coefficients are presented in Tables 1-4. Values of k_d decreased with increase in initial MB concentration and ranged from 0.48-4.466. In

general high k_d values illustrate a better adsorption mechanism, which is related to an improved bonding between the MB and the adsorbent particles (Demirbas *et al*, 2004). The

kinetic data obtained for Dausha 1:3 fits the intra-particle diffusion model better given the high correlation coefficients ($r=0.934-0.997$) obtained. On the other hand, the intercept of the plots, I reflect the thickness of the boundary layer Abdelwahab (2007). The larger the intercept, the greater is the contribution of the surface sorption in the rate-limiting step (El-Latif *et al*, 2010).

CONCLUSION

Kinetic studies were carried out using activated carbons prepared from mango seed shell on the adsorption of colour and phenol from wastewater. Kinetic data generated from these studies were used for kinetic modelling in order to determine the rate and mechanism of adsorption.

Adsorption was best fitted by the pseudo-second order kinetic model for both colour and phenol adsorptions with correlation coefficients, r generally greater than 0.99 for all the experimental carbons studied. This suggests that the rate-limiting step may be chemisorptions involving valence forces through sharing or exchange of electrons between adsorbent and MB. The mechanism of adsorption was rather complex and is probably a combination of external mass transfer and intra-particle diffusion given that the linear intra-particle diffusion kinetic plots do not pass through the origin. These results revealed that MSSAC is more effective for the adsorption of colour than phenol from wastewater.

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