



Effect of chlorine substitution on the removal of phenols by activated carbon

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Abstract

A comparison of the removal of substituted phenols (2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol) with phenol using adsorption process on activated carbon has been investigated. The adsorption data was modeled using Langmuir and Freundlich equations and the Langmuir model was found to be the best fit. The removal of phenols by activated carbon followed a trend based on number of chlorine substitution with order: phenol < 2-chlorophenol < 4-chlorophenol < 2,4-dichlorophenol. Substantial uptake of the phenols on activated carbon was observed and was found to be 0.83, 0.91, 0.93 and 1.51 mmol/g for phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol, respectively. Pseudo-first order and pseudo-second order models were used to analyse the kinetic data and the process was found to follow pseudo-second order kinetic model.

Keywords: *activated carbon, adsorption, chlorophenols, phenol, kinetics*

Introduction

Phenol and chlorophenols are considered as highly toxic environmental contaminants that remain persistent in atmosphere (Kakavandi *et al.* 2016). They act as starting materials or as intermediates in many chemical industries like resin, dyes, plastics, pharmaceutical, pulp and paper manufacturing industries (Priya and Madras 2006). Chlorophenols are used as herbicides, biocides, fungicides and are even available in water through drinking water chlorination (Quintana and Ramos 2008). Consumption of water containing phenol causes spasms, severe renal insufficiency and even death (Gundogdu *et al.* 2012). Furthermore, even at low level they act as irritants and may affect the central nervous and respiratory systems, besides this at a higher dose phenol can induce cancer too (Priya and Madras 2006). The degree of chlorination and chlorine atom position relative to the hydroxyl group affects the toxicity of chlorophenols (Czaplicka 2004). It is worthwhile mentioning that this degree of chlorination and the chlorine atom position may play an important role in their removal too. Further, it is interesting to note that chlorophenols with less number of chlorine are extremely hydrophilic, consequently they get easily

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dispersed in aquatic environment while more chlorinated chlorophenols spread less, even though they generally persist for longer time (Quintana and Ramos 2008). The chlorophenols are weakly acidic in nature and may permeate through human skin and also get freely absorbed by gastrointestinal tract, producing toxic effect (Domínguez-Vargas *et al.* 2009). Among various methods available for the removal of phenols adsorption process is a very effective technique and is generally used for the elimination of these type of organic pollutants from waste effluents. Higher efficiency and insensitivity to toxic substances compared to the other conventional methods of water purification has made this process much more popular (Mehta *et al.* 2015). Adsorption is a surface boundary phenomenon that involves the enrichment of the chemical species from the fluid phase on to the surface of liquid or solid (Worch 2012). The adsorption process either results from the Van der Waals interaction or it may involve chemical interaction (Dąbrowski 2001). For adsorption process owing to well-developed porosity, large surface area and variable surface chemistry activated carbons are better choice as adsorbents for the removal of organic pollutants like phenols (Cotoruelo *et al.* 2007). The objectives of present work are to make a comparative study of the removal of substituted phenols (2-chlorophenol, 4-



chlorophenol and 2,4-dichlorophenol) and phenol using activated carbon developed from lignin and to investigate the effect of number and position of chlorine on the mechanism of adsorption. Furthermore, the aim is also to study the effect of different parameters such as contact time, initial phenol concentration and temperature. The parameters related to the adsorption isotherms and kinetics for the adsorption of phenols (phenol and chlorophenols) on activated carbon developed from lignin has also been evaluated.

Material and Methods

Phenol was purchased from Merck Pvt. Ltd. and 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol were purchased from Sigma Aldrich. The basic structural characteristic and selected properties of chlorophenols and phenols are listed in Table 1. Stock solutions ($1 \times 10^{-2} \text{M}$) of phenols were prepared by dissolving the desired amount of phenol and chlorophenols in double distilled water. The stock solutions were diluted to get the desirable experimental concentration. The activated carbon utilized in the study was produced from a kraft lignin sample obtained from Lignotech Ibérica (Spain). For the production of the activated carbon the methodology as discussed elsewhere (Carrott *et al.* 2008) has been used. Almost 5g of lignin was placed in a ceramic boat and positioned in the central constant temperature zone of a conventional horizontal tubular furnace. Carbonisation was carried out by heating to 750°C at a rate of 8°Cmin^{-1} under a constant N_2 flow of $85\text{cm}^3\text{min}^{-1}$ and maintaining for 30min. Physical activation in CO_2 was carried out by switching to a CO_2 flow of $85\text{cm}^3\text{min}^{-1}$ at same temperature (750°C) for 30 min and thereafter switching back to the N_2 flow and allowing to cool to below 50°C before removing the AC from the furnace and storing in a sealed sample flask. The Brunauer-Emmett-Teller (BET) surface area of the activated carbon so developed was found to be $605 \text{ m}^2/\text{g}$ by N_2 adsorption.

Batch adsorption studies

Batch technique was used for the adsorption of phenols (phenol and chlorophenols) from aqueous solutions using the activated carbon synthesised from kraft lignin. For this 0.01g of the activated carbon was added to the stoppered glass tubes

containing 10 ml of solution with varying concentration. The samples were agitated in a thermostatted shaker at desired temperature until the equilibrium was achieved. The concentration of phenols and chlorophenols left unadsorbed in aqueous solutions were determined by using Agilent Cary 60 UV-Vis spectrophotometer at wavelength 274, 280, 285 and 270 nm for 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and phenol, respectively. All the experiments were carried out in duplicate and the mean value was used in all cases. The equilibrium adsorption capacity q_e (mmol/g) was calculated by using the following equation.

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations in the solution (mol/L), respectively, V is the solution volume (L), and W is the mass (g) of adsorbent used.

Results and Discussion

Effect of contact time

For the determination of appropriate contact time in order to remove phenol and chlorophenols (2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol) the adsorption capacity of activated carbon developed from lignin was determined as a function of time and is shown in Fig.1. It can be observed from the Figure that during initial stage there is a rapid increase in adsorption followed by long period of much slower uptake until the equilibrium was achieved. This is due to the fact that during the initial stage of contact time a large number of free adsorption center are available for adsorption but after a interval of time residual free adsorption center were hard to be occupied due to the repulsion between the adsorbate molecule on the solid and bulk phases (Tan *et al.* 2009). The maximum amount of phenol and chlorophenols was removed in ~ 60 min and thereafter equilibrium was achieved in approximately 240 min. A small difference observed may be explained by the fact that the time of equilibration seems to be controlled by the molecular size of phenols. Large molecules may take comparatively longer time. However, the contact time was kept at 300 min for all molecules in further studies.

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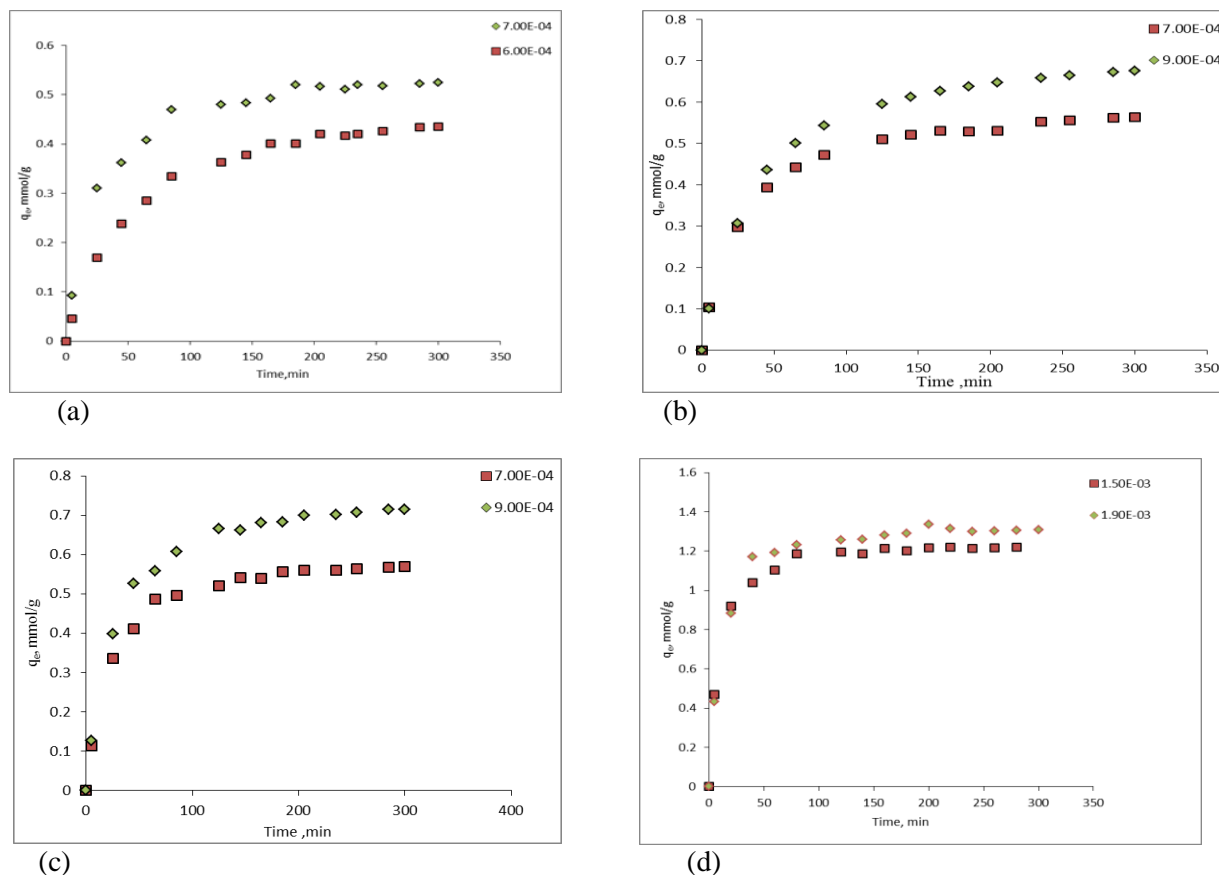


Fig.1 Effect of contact time on the uptake of a) phenol b) 2-chlorophenol c) 4-chlorophenol and d) 2,4-dichlorophenol on activated carbon developed from lignin

Effect of initial phenol concentration

The effect of variation in the initial concentration on the adsorption of phenol and chlorophenols was studied. The amount adsorbed at two different concentrations is presented in Fig.1, which shows that the amount of phenols adsorbed increases on increasing the concentration. However, the percentage adsorption was found to decrease which may be due to the fact that on increasing the concentration adsorption centers of the adsorbent get saturated whereas, on the other hand the accessibility of centers available for adsorption are more at lower concentration for the binding of the adsorbate molecule.

Adsorption isotherms

Adsorption isotherm describes the relationship between the concentration of the adsorbate on the solid phase and in the liquid phase (Jagadeesh Babu

et al. 2010). The adsorption isotherm obtained for chlorine substituted phenols (2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol) along with phenol was studied as a function of concentration and the adsorption isotherms (at 25 and 45°C) obtained on activated carbon developed from lignin are shown in Fig. 2 and 3. The experimental adsorption values observed from the figure 2 at 25°C were found to be 0.83, 0.91, 0.93 and 1.51mmol/g for phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol, respectively. These values obtained are compared with other activated carbons too (Table 1) in order to assess the removal efficiency of the present adsorbent and process. The results clearly show the process to be at par with other materials and justify the applicability of the process. Conventionally used models Langmuir as well as Freundlich were used to analyse the adsorption isotherms. Langmuir isotherm model

assumes monolayer adsorption on surface containing finite number of energetically equivalent identical sites and is represented by the following equation (Langmuir 1918).

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \quad (2)$$

where q_e is the amount of the adsorbate adsorbed at equilibrium concentration, q_m is the theoretical maximum adsorption capacity, b the Langmuir adsorption constant and C_e the equilibrium concentration of the adsorbate.

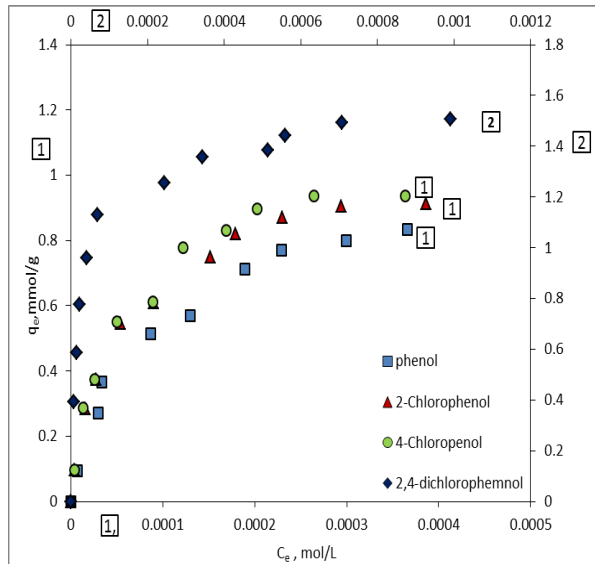


Fig.2 Adsorption isotherms of phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol on activated carbon developed from lignin at 25 °C.

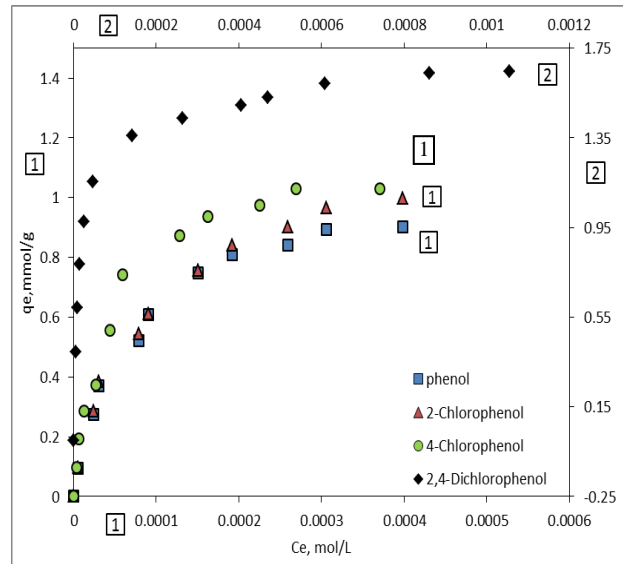


Fig.3 Adsorption isotherms of phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol on activated carbon developed from lignin at 45°C

Table 1- Adsorption capacities of different adsorbents for the removal of phenols

S.no.	Adsorbate	Adsorbent	Surface area (m ² /g)	Amount adsorbed (mg/g)	Reference
1	Phenol	Activated carbon from jackfruit peel	115.25	144.9	(Jain and Jayaram 2007)
		Activated carbon from kenaf	493	140.84	(Aber <i>et al.</i> 2009)
		Activated carbon(AC-P)	940	106.5	(Fierro <i>et al.</i> 2008)
		CAC 2 Activated carbon developed from lignin	620 605	73.91 78.47 (0.83 mmol/g)	This study
2	2-chloro phenol	Granular activated carbon	954	294	(Hossain and McLaughlan 2012)
		Activated carbon from jackfruit peel	115.25	243.9	(Jain and Jayaram 2007)
		Ricinus communis pericarp activated carbon		71.43	(Adane <i>et al.</i> 2015)
		Activated carbon developed from lignin	605	117.5 (0.91 mmol/g)	This study



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3	4-Chloro Phenol	Activated carbon from jackfruit peel	115.25	277.7	(Jain and Jayaram 2007)
		Activated carbon (CWZ)	977	322	(Lorenc-Grabowska <i>et al.</i> 2010)
		Activated carbon CWZ N ₂	940	369	(Lorenc-Grabowska <i>et al.</i> 2010)
		Activated carbon CWZ NH ₃	914	263	(Lorenc-Grabowska <i>et al.</i> 2010)
		Activated carbon from waste coconut shells (csac)	935.24	72.7	(Radhika and Palanivelu 2006)
		Commercial activated carbon	838.45	134.09	(Radhika and Palanivelu 2006)
		Granular activated carbon	954	319	(Hossain and McLaughlan 2012)
		Carbon derived from refuse derived fuel (RDFN1)	898	416	(Wu <i>et al.</i> 2014)
		Activated carbon developed from lignin	605	119 (0.93mmol/g)	This study
4	2,4dichlorophenol	Activated carbon from jackfruit peel	115.25	400	(Jain and Jayaram 2007)
		Granular activated carbon	954	467	(Hossain and McLaughlan 2012)
		Activated carbon from Prosopis africana seed hulls	1085.9	380.7	(Garba and Rahim 2016)
		Activated carbon fiber	702	372	(Wang <i>et al.</i> 2007)
		Activated carbon developed from lignin	605	245 (1.51mmol/g)	This study

In order to define the favorability of adsorption process a dimensionless constant separating factor or equilibrium parameter 'R_L' is also calculated (Weber and Chakravorti 1974) using the following equation

$$R_L = \frac{1}{1 + b C_0} \quad (3)$$

where C₀ is the initial concentration and b the Langmuir adsorption constant. The R_L value indicate whether the adsorption is favourable (0 < R_L < 1), linear (R_L=1), irreversible (R_L=0), or unfavourable (R_L> 1). As the R_L values for all experiments were observed between 0 and 1, the adsorption can be said to be favorable in all cases. Besides Langmuir, Freundlich isotherm has also been widely used in order to study the adsorption process. Freundlich equation is an empirical equation that is very useful as it also accurately describes adsorption data. The well-known

logarithmic form of the equation (Freundlich 1906) is given by:

$$\log q_e = \log k_F + (1/n) \log C_e \quad (4)$$

where q_e is the amount of the adsorbate adsorbed at the equilibrium concentration, k_F and n are the constants that define the adsorption capacity and adsorption intensity, respectively. The plots of Langmuir (1/q_e versus 1/C_e) and Freundlich (log q_e versus log C_e) for the adsorption of phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol on activated carbon from lignin at temperatures 25 and 45°C according to their linear form are shown in Figs. 4 and 5. The constant calculated from the linear form of the equations 3-4 are given in Table 2. It can be observed from Table that the experimental values at these temperature were found to be in well agreement with the theoretical value obtained from the Langmuir



model. Moreover, the correlation coefficients are found to be better for Langmuir model in

comparison to the Freundlich model thereby indicating the process to conform Langmuir model.

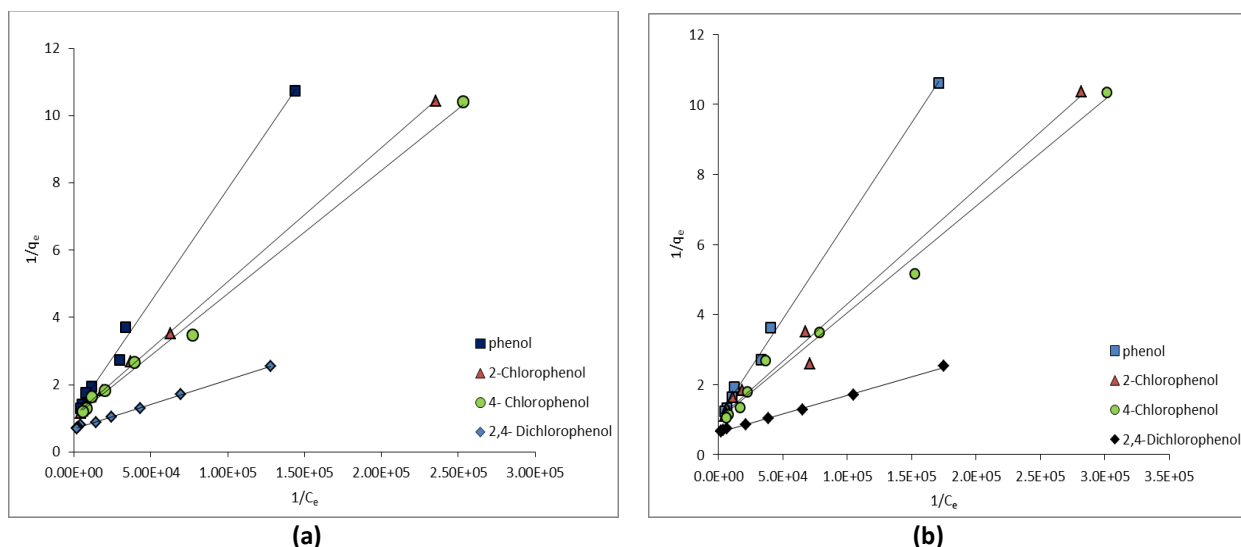


Fig.4 Langmuir adsorption isotherms of phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol on activated carbon developed from lignin a) 25 °C and b) 45 °C.

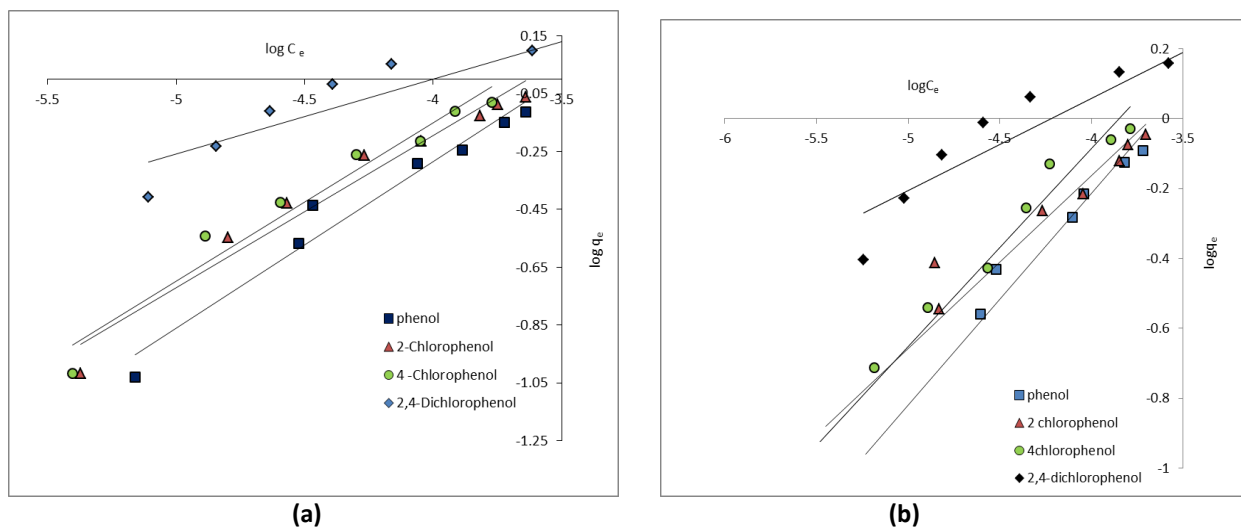


Fig.5 Freundlich adsorption isotherms of phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol on activated carbon developed from lignin a) 25°C and b) 45°C

Mechanism of adsorption and effect of chlorine substitution on the removal

The adsorption capacity of phenol and chlorophenols from Fig. 2 was found to follow the order: 2,4-dichlorophenol > 4-chlorophenol > 2-chlorophenol > phenol. This is due to the fact that chlorine is an electron withdrawing group that

deactivates the aromatic ring and makes it partially positive in nature, as the number of chlorine atom increase this effect was found to be increase thereby resulting in the formation of donor-acceptor interaction between the oxygen containing groups on carbon surface and the aromatic ring. Furthermore, the solubility (Table 3) of phenol and


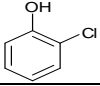

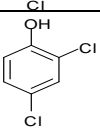


chlorophenols is found to be in the order: phenol > 2-chlorophenol > 4-chlorophenol > 2,4-dichlorophenol, which may also be the factor for the adsorption to be in the reverse order, and this explains the higher adsorption capacity of 4-chlorophenol too in comparison of 2-chlorophenol though both contains one chloro group only.

Table 2: Langmuir and Freundlich isotherm constants and correlation coefficients for phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol adsorption onto activated carbon developed from lignin at different temperatures

Types of Adsorbates	Temperature	Langmuir			Freundlich		
		q_m (mmol/g)	b (L/mmol)	R^2	K_f (mmol/g)	n	R^2
Phenol	25°C	0.90	1.66×10^4	0.996	107.15	1.73	0.961
	45°C	0.95	1.87×10^4	0.997	161.06	1.65	0.972
2-chlorophenol	25°C	0.93	2.71×10^4	0.999	80.87	1.90	0.959
	45°C	0.98	3.12×10^4	0.988	65.71	2.02	0.928
4-chlorophenol	25°C	0.96	2.84×10^4	0.966	109.39	1.83	0.956
	45°C	0.99	3.33×10^4	0.991	153.85	1.76	0.968
2,4-dichlorophenol	25°C	1.45	4.76×10^4	0.998	10.96	3.85	0.878
	45°C	1.58	5.97×10^4	0.997	13.04	3.79	0.873

Table 3- Structural characteristic and selected properties of phenol and chlorophenols

Phenols	Molecular weight	Structure	λ_{max} (nm)	Solubility ^a (g/L of water)	pKa ^a
Phenol	94.11		270	93	9.89
2-chlorophenol	128.56		274	28	8.52
4-chlorophenol	128.56		280	27	9.37
2,4-dichlorophenol	163		285	4.5	7.90

^a (Dąbrowski *et al.* 2005)

This behaviour is usual and expected since molecules if have less solubility i.e., lesser affinity for water, tend to get adsorb more (Moreno-Castilla *et al.* 1995).

Effect of temperature and free energy change

A series of experiments have been conducted at higher temperature (45°C) too keeping the rest parameters constant in order to study the effect of

temperature on adsorption and the results are shown in Fig. 3. The experimental adsorption values observed from the figure 3 were found to be 0.91, 1.00, 1.02 and 1.65 mmol/g for phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol, respectively. It can be seen from the Figures 2 and 3 that amount adsorbed increases on increasing the temperature indicating the process to be endothermic in nature. The reason for this

change can be explained on the basis of hydrogen bonding (Jain *et al.* 2004). Phenol molecules forms hydrogen bonds with water and thereby makes them appreciable soluble in water. However, when temperature is increased these bonds broke which in turn makes phenols less soluble and therefore, they exhibit higher tendency to go to the activated carbon surface and get adsorbed rather than remaining in the solution. This results in more adsorption at higher temperatures. Gibbs free energy change (equation 5) was also calculated at different temperatures using Langmuir constant and the value were found to be in the range of -24.1 to -29.1 kJ/mol.

$$\Delta G^\circ = -RT\ln(b) \quad (5)$$

The negative value of ΔG° obtained at different temperatures suggests that the process is spontaneous and thermodynamically favorable.

Adsorption kinetics

Kinetic study for the adsorption of phenol and substituted phenols (2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol) has been carried out up to 300 min. The pseudo-first order and pseudo-second order models were used for the kinetic studies. The pseudo-first order (Lagergren 1898) has been one of the widely used rate equations in the liquid adsorption and is given by:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

where q_e and q_t are amount adsorbed at equilibrium and at time t respectively and k_1 the pseudo-first order rate constant. Kinetic constants were obtained by plotting $\log(q_e - q_t)$ versus time t in Fig. 6 and the values for kinetic parameters are shown in Table 4.

Table 4- Kinetic parameters for the adsorption of phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol on activated carbon developed from lignin.

Types of adsorbates	C ₀ (mol/L)	q _e (exp) (mmol/g)	Pseudo-first order			Pseudo-second order		
			q _e (cal) (mmol/g)	K ₁ (1/min)	R ²	q _e (cal) (mmol/g)	K ₂ (g/mmol min)	R ²
Phenol	7.0 × 10 ⁻⁴	0.525	0.323	1.18 × 10 ⁻³	0.896	0.573	7.25 × 10 ⁻²	0.998
2-chloro phenol	7.0 × 10 ⁻⁴	0.563	0.384	7.83 × 10 ⁻³	0.906	0.603	6.86 × 10 ⁻²	0.999
4-chloro phenol	7.0 × 10 ⁻⁴	0.569	0.315	9.21 × 10 ⁻³	0.891	0.608	7.82 × 10 ⁻²	0.999
2,4-dichloro phenol	1.5 × 10 ⁻³	1.22	0.387	1.2 × 10 ⁻²	0.838	1.258	1.051 × 10 ⁻¹	0.999

Besides pseudo-first order rate equation, pseudo-second order equation (Ho and McKay 1998) was also applied to study the kinetics of process. The equation used is given as:

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

where q_e and q_t are the amount adsorbed at equilibrium and time t , respectively, k_2 is the pseudo-second order rate constant and $K_2 q_e^2 = h$ the initial adsorption rate. A plot made between the t/q_t vs t is presented in Fig.7 and the values of k_2 and q_e are determined from it. The experimental

data and parameters of both the models are given in the Table 4. The correlation coefficients (R^2) values obtained (Table 4) for the pseudo-second order were found to be high compared to the pseudo-first order. Further, the experimental q_e value was found to be in well agreement with the calculated value obtained from the pseudo-second order model. Therefore, it can be concluded that pseudo-second order kinetic model fitted well for adsorption of substituted phenols (2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol) as well as phenol on activated carbon developed from lignin.



Conclusion

The current study shows that the removal of phenols (phenol as well as chlorophenols) can be carried out efficiently by activated carbon using adsorption process. The chlorine substitution play

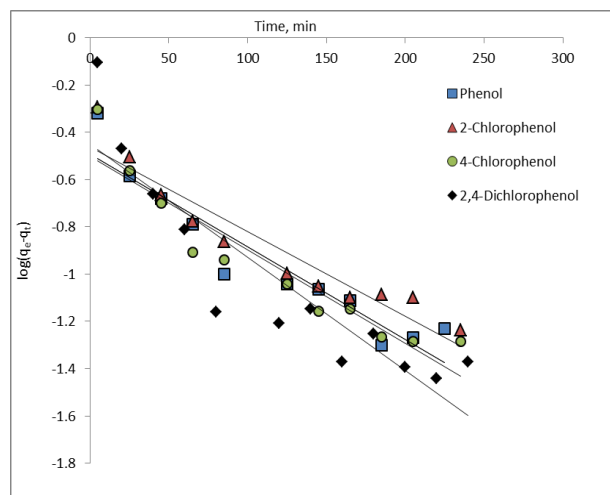


Fig.6 Pseudo-first order kinetics for adsorption of phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol on activated carbon developed from lignin

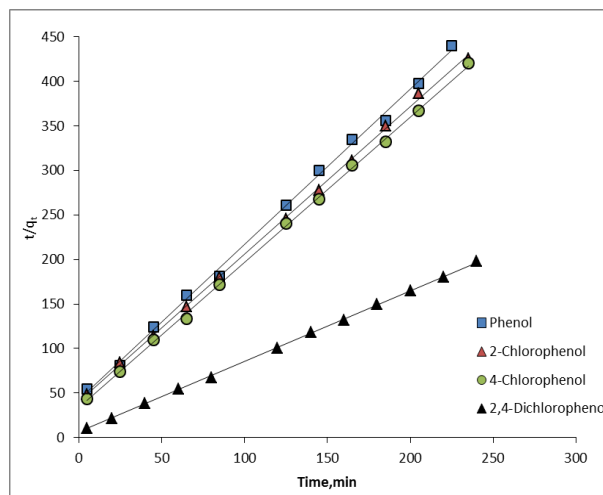


Fig.7 Pseudo-second order kinetics for adsorption of phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol on activated carbon developed from lignin

an important role in the removal of phenols by activated carbon following an order as phenol < 2-chlorophenol < 4-chlorophenol < 2,4-dichlorophenol. Significant adsorption of the phenols on activated carbon was observed and was found to be 0.83, 0.91, 0.93 and 1.51 mmol/g for phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol, respectively. The process was found to fit Langmuir model and followed pseudo-second order kinetics.

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