Original Research Paper

Preparation, characterization and phenol adsorption capacity of activated carbons from *African beech* wood sawdust

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ABSTRACT: In the present study, different activated carbons were prepared from carbonized *African beech* wood sawdust by potassium hydroxide activation. The activated carbons were characterized by brunauer–emmett–teller, scanning electron microscope, fourier transform infrared spectroscopy, and thermogravimetric analyzer. The phenol adsorption capacity of the prepared carbons was evaluated. The different factors affecting phenol's removal were studied including: contact time, solution pH and initial phenol concentration. The optimum phenol removal was obtained after a contact time of 300 min. and at an initial phenol solution pH 7. The maximum removal percentages were determined at 5 mg/L initial phenol concentration as 79, 93, 94 and 98% for AC0, AC1, AC2 and AC3; respectively. The adsorption of phenol on *African beech* sawdust activated carbons was found to follow the Lagergren first order kinetics and the intraparticle diffusion mechanism gave a good fit to the experimental data. The isothermal models applied fitted the experimental data in the order: Langmuir> Dubinin–Radushkevich> Freundlich and Temkin.

KEYWORDS: *Activated carbon; Brunauer–emmett–teller (BET); Fourier transform infrared spectroscopy (FTIR); Isothermal modeling; Kinetics surface characteristics; Potassium hydroxide (KOH); Thermogravimetric analyzer (TGA)*

INTRODUCTION

Wastewater containing phenolic compounds presents a serious discharge problem due to their poor biodegradability, high toxicity and ecological aspects. Phenolic compounds are frequent contaminants of ground water because of their wide use in industrial sectors (Sabio *et al.,* 2001). They are widely present in many effluents such as those generated from coal tar, plastics, leather, paint, pharmaceutical, steel, textile, timber, paper pulp, insecticides, pesticides and oil refineries (Podkoscielny *et al.,* 2003). Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health (Nagda *et al.,* 2007). The ingestion of water contaminated by phenols in the human body causes protein degeneration, tissue erosion and paralysis of the central nervous system and also damages the kidney, liver and pancreas (Yan and Guixiang, 2009). Thus removing phenols from industrial effluents before discharging into the water stream is a necessity. There are many methods such as oxidation, precipitation, ion exchange, solvent extraction and adsorption for removing phenols and phenol derivatives from aqueous solutions (Aksu and Yener, 2001; Tseng and Tseng, 2005). In review of wastewater treatment containing phenolic compounds,

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it was found that adsorption by activated carbon is considered as a useful treatment technique (Moreno-Castilla, 2004) and one of the best available environmental control technologies (Lin and Cheng, 1999). Activated carbons are considered to be good and effective adsorbents for the removal of phenol from wastewater because of their large surface area, porous nature, high adsorption capacity, high purity and availability.

Many recent studies reported the development of activated carbon from cheap and readily available materials. Activated carbons have been prepared from corncob (Tseng and Tseng, 2005), sugar beet bagasse (Onal *et al.,* 2007), apricot shell (Karagozoglu *et al.,* 2007), sunflower seed hull (Thinakaran *et al.,* 2008), agricultural waste material (Singh *et al.,* 2008), bagasses (Juang *et al.,* 2002), rubber seed coat (Rengaraj *et al.,* 2002), coconut shell (Hu and Srinivasan, 1999), apricot stone shells (Daifullah and Girgis,1998) oil palm fibre (Tan *et al.,* 2007) , bamboo (Hameed *et al.,* 2007), coconut husk (Tan *et al.,* 2008) and *Heveabrasiliensis* seed coat (Hameed and Daud, 2008).Generally activated carbons are prepared by two different activation processes, either by physical or chemical activation. The chemical activation is preferred over physical activation for its lowered activation temperature and increased yield (Ioannidou and Zabaniotou, 2007; Adinata*et al.,* 2007).

The aim of the presents study was to use *African beech* wood sawdust for the production of activated carbons and to evaluate their characteristical properties and their adsorption capacities for phenol removal from aqueous solutions. This study has been performed in Egypt during 2015.

MATERIALS AND METHODS
Materials

Sawdust was collected from Egyptian furniture factories. Phenol (Fluka) was used without further purification. Stock solutions were prepared by dissolving 1.0 g of phenol individually in 1 L of double distilled water. This stock solution was used to prepare the different diluted solutions of phenol used in the experiments. HCl and NaOH used to adjust solutions pH were obtained from Sigma.

Methods
Adsorbents Preparation

Activated carbons used in the present study were prepared following the procedure described by Wu *et*

al., (2012) with some modifications. The sawdust was washed several times with deionized water to remove surface impurities, and then it was oven dried at 105°C for 24 h.The dried sawdust was immersed in 25 wt% H_2SO_4 overnight, and then was carbonized in vacuum oven at 290 ºC for 2 h. It was then washed with deionized water until the water was neutral. At this stage, it was called the sawdust char (AC0). The resulting char was immersed in potassium hydroxide solution (KOH), with the KOH/char weight ratio of 1, 2, and 3, respectively, and was finally activated at 780 ºC for 1 h. The prepared carbons were accordingly denoted as, AC1, AC2, and AC3; respectively.

Adsorbents characterization

The adsorbents surface functional groups were obtained by the fourier transform infrared spectroscopy (FTIR) analysis over the range of 500–4000 1/cm using a Nicolet, AVATAR FTIR-370 Csl instrument. The microstructure of the adsorbents was examined using a scanning electron microscope (SEM, Quanta 250- FEI). The adsorbents surface properties were determined with an automatic adsorption instrument (Porous materials Co., BET-202A) in order to determine surface areas and total pore volumes. Thermogravimetric analysis of the adsorbents was also carried out using a thermogravimetric analyzer (TGA-Q 500).

Adsorption experiments

Batch adsorption studies were carried out at room temperature. The effect of contact time on phenol removal was investigated by mixing a known volume of phenol solution with a known adsorbent weight in capped conical flasks for different time intervals (30-900 min). The solution-adsorbent mixtures were stirred at 100 rpm in a shaking water bath at 25°C. At the end of each time interval the samples were filtered through Whatman No. 50 filter paper (2.7µm size particle retention) to eliminate any fine particles. The effect of each of the operational parameters affecting phenol adsorption was studied. Batch studies were performed as function of adsorbent dosage ranging from (0.1-2.5g), solution pH (2-10) and phenol concentration (5-100 mg/L) in separate experiments. The concentration of phenol was determined by measuring absorbance using UV–vis spectrophotometer (Shimadzu UV-1601 Spectrophotometer, Japan) at 270 nm.

Phenol removal percentages were determined using equation1.

$$\text{Removal } \% = (C_i - C_f) * 100/C_i \qquad (1)$$

Where, C_i and C_f are the initial and final concentrations of phenol (mg/L) in the solution Adsorption capacity was calculated using equation 2.

$$Q = (C_i - C_f) * V/W \qquad (2)$$

Where Q is the adsorption capacity (mg/g), C_i is the initial phenol concentration in solution (mg/L), C_f is the equilibrium phenol concentration (mg/L), V is the volume of metal ion solution (L) and W is the weight of the adsorbent (g).

The kinetics of analyzing adsorptive uptake of phenol from aqueous solution at different time intervals was studied using four kinetic models (namely, pseudo-ûrst- order, pseudo-second-order, the Elovich equation and intra-particle diffusion). Adsorption isotherm studies were carried out using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D-R) isothermal models.

RESULTS AND DISCUSSION
Physical properties of KOH-activated carbons prepared from African beech sawdust

Table 1 gives the physical properties of AC0 (the carbon without KOH activation), AC1, AC2 and AC3 prepared by KOH- activation using different KOH/char ratios. As seen from Table.1 the *total surface area (S_{tot})* was significantly improved upon KOH activation of the sawdust. The *(S_{tot})* value of KOH-activated carbons increased with increasing KOH/char ratio, a similar behavior was previously reported by Wu *et al., (2005)*. The maximum S_{tot} value obtained in the present study for AC3 (1553.8 m²/g) was better than previously reported S_{tot} values of commercial activated carbon

(Kumar *et al.,* 2006), steam activated carbon from rubber wood sawdust (Kumar *et al.,* 2006), sawdust and neem bark (Naiya *et al.,* 2009). The total pore volume V_{tot} increased from 0.033 to 1.325cm³/g with increasing KOH/char ratio. Comparing V_{micro} and V_{meso} values it is clear that the prepared adsorbents exhibited significantly developed micropore and mesopore structures, with a higher portion of mesopores than micropores that were observed upon KOH activation. During adsorption, macro and mesopores allow rapid transport of the adsorbate into the interior of the carbon for subsequent diffusion into the micropore volume (Galiatsatou *et al.,* 2001).

According to (Galiatsatou *et al.,* 2001), the pores of activated carbons are classified into three groups depending on pore width (pw): micropores (pw <20A°); mesopores (20A° < pw< 500A°); macropores (pw> 500A°). As seen from Table 1 the pore diameters of the prepared adsorbents ranged from 40.2 to 115.5A° confirming their mesoporous structures.

Scanning electron microscope (SEM) studies

The SEM enables the direct observation of the changes in the surface microstructures of the adsorbents due to the modiûcation (Jain *et al.,* 2010).

Fig.1 shows the SEM micrographs of the char produced from the African beech sawdust (AC0), and the activated carbons AC1, AC2 and AC3 chemically activated by different char: KOH impregnation ratios 1:1, 1:2 and 1:3; respectively.

The SEM photo of AC (Fig. 1 a) shows a ruptured surface with long ridges resembling a series of parallel lines and a small number of pores (Asadullah *et al.,* 2010). The chemical activation with KOH allowed the development of pores with different sizes on the char surface. As can be seen from (Fig. 1 b) a number of

Table 1: Physical properties of carbons derived from *African beech* sawdust by KOH activations

Characteristics	AC0	AC1	AC2	AC3
Color	Brown	Black	Black	Black
S_{mic} micropore surface area (m²/g)	114.600	863.700	913.600	1046.900
S_{mes} mesopore surface area (m²/g)	251.700	373.100	421.200	506.900
S_{tot} total BET surface area (m²/g)	366.300	1236.800	1334.800	1553.800
V_{micro} micropore volume of the adsorbent (cm³/g)	0.010	0.219	0.292	0.317
V_{meso} mesopore volume of the adsorbent (cm³/g)	0.023	0.564	0.839	1.008
V_{tot} total pore volume of the adsorbent (cm³/g)	0.033	0.783	1.131	1.325
V_{meso}/ V_{tot} (%)	69.700	72.000	74.200	76.100
Average pore width (Å)	115.500	84.400	63.800	40.200
Production yield of carbon (%)	50.700	49.400	47.200	46.800
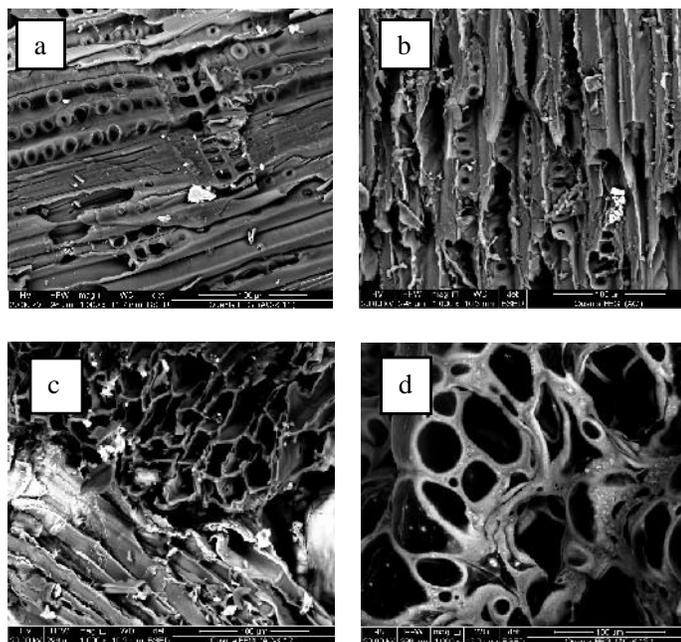
Fig. 1:SEM images of (a) AC0, (b) AC1, (c) AC2 and (d) AC3 (1000×)

small sized pores has been developed on the surface of AC1. The pores build-up and pores size increased by increasing the char: KOH ratio of activation. The surface of AC2 (Fig.1 c) shows large pores, non-homogenous in size and randomly distributed on the carbon's surface. Large and well-developed pores were clearly found on the surface of the activated carbon AC3 as seen in (Fig. 1 d). It can be concluded that surface modiûcation of sawdust contributed positively to the pores development (Jain *et al.,* 2010).

According to Tan *et al.,* (2008); the development of pores on the surface of the activated carbon, might be due to the activation process used, which involved both chemical and physical activating agents of KOH and CO_2. Pore development in the char during pyrolysis was also important as this would enhance the surface area and pore volume of the activated carbon by promoting the diffusion of KOH and CO_2 molecules into the pores and thereby increasing the KOH–carbon and CO_2–carbon reactions, which would then create more pores in the activated carbon. The differences in the surface structure of the activated carbons produced by chemical activation with KOH could be attributed to the removal of considerable organic by-products and minerals present in the sawdust upon activation (Kalavathy *et al.,* 2010).

FTIR analysis

According to Hanafiah *et al.,* (2012), sawdust is known to contain lignin, hemicellulose, cellulose and tannin as the major components. Thus various types of functional groups such as carboxyl, alcohols, amines and phenolic might be involved during the adsorption process. The FTIR spectra of the different adsorbents prepared from African beech sawdust are presented in Fig . 2.

The spectra of the four studied adsorbents show bands in the region (3500–3200 cm^{-1}) characteristic for (-OH) stretching vibration in hydroxyl groups. These bands are very weak indicating that upon carbonization and chemical activation of the sawdust some types of bond cleavage occurs, leading to dehydration and elimination reactions that release volatile products such as water, acetic acid, methanol and other chemical substances (Ljupkoviæ *et al.,* 2011). The peak observed in the spectra of AC0 at 1712.48 1/cm assigned to C=O carbonyls disappeared in the KOH- activated carbon samples.

The peaks at 1650–1450 cm^{-1} present in the spectra of all prepared adsorbents are assigned to aromatics C=C stretching; and those peaks at 1000–1100 1/cm are assigned to C–O and C–O–C stretchings (Jibril *et al.,* 2007). The peaks around 600-900 1/cm in the spectra
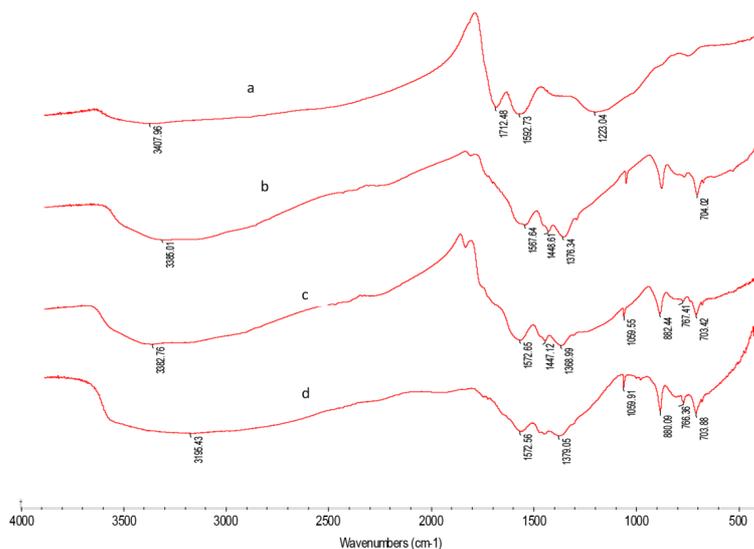
Fig.2: FTIR spectra of (a) AC0, (b) AC1, (c) AC2 and (d) AC3
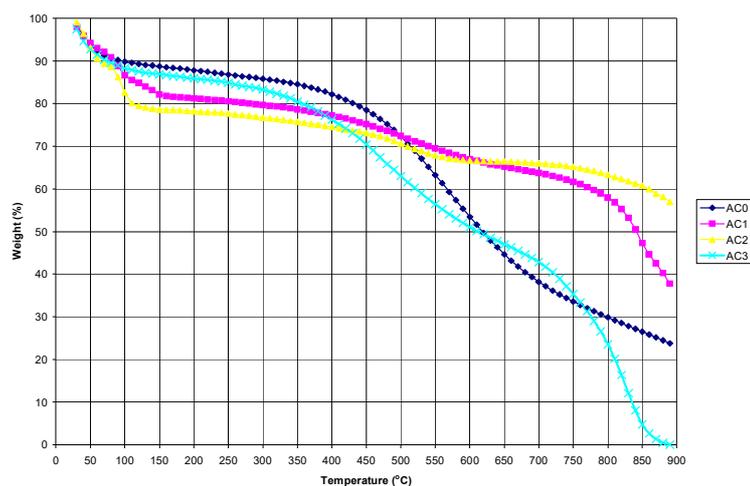
Fig. 3: TGA graphs of the activated carbons prepared from *African beech* sawdust

of AC1, AC2 and AC3 were assigned to bending of hydrogen in various locations in the aromatic rings (Jibril *et al.,* 2007).

Thermogravimetric Analysis (TGA)

TGA analysis of the activated carbons was obtained by heating the samples from 30 to 900 °C at a ramping rate of 10ºC/min under nitrogen gas atmosphere. The TGA curves of the different activated carbons prepared from African beech sawdust are presented in Fig. 3. At temperatures above 100 ºC, chemical bonds begin to break. The rate at which the bonds are broken increases as the temperature increases. The weight loss from room temperature to 130 ºC observed in the thermographs corresponds to the release of water vapor (Seey and Kassim, 2012). Upon rapid heating, the carbohydrates (cellulose and hemicellulose) break down to provide low molecular weight volatile products.

Another weight loss step occurred from above 100 ºC to around 400 ºC. This step was attributed to the removal of volatile matter which corresponded to the decomposition of cellulose, hemicellulose and lignin (Kalderis *et al.,*2008).The broad weightloss step that
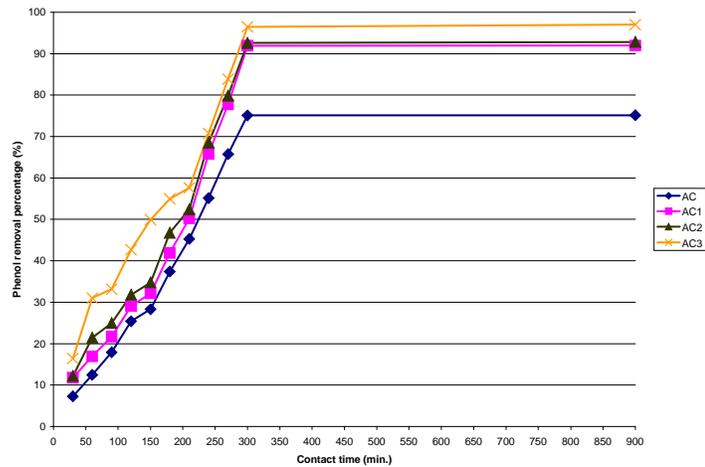
Fig. 4: Effect of contact time on phenol removal by adsorption onto AC0, AC1, AC2 and AC3

occurs above 350 ºC, is due to carbonization process which may be attributed to cellulose, hemicellulose and lignin intermediates being transformed to gaseous materials and tars (Kalderis *et al.,* 2008).The observed weight loss taking place at temperatures above 800 ºC might be due to a possible melting of the traces of potassium carbonate, contained in the carbon matrix, and its possible decomposition into CO_2 (El-Hendawy, 2009).

Effect of contact time and kinetic studies

The relationship between contact time and phenol removal obtained by the activated carbons prepared from *African beech* sawdust is presented in Fig. 4 for an adsorbent dosage of 5 g/L, initial phenol concentration of 25 mg/L and at a solution pH =7. It can be seen from the Fig. 4 that the percentage phenol removal started very slow and then increased gradually with increasing the contact time until equilibrium was attained. It can be seen from Fig.4 that the removal of phenol by the studied adsorbents remained almost unchanged from 300 to 900 min. Thus for further experiments the contact time was kept at 300 min.

The importance of kinetic modeling has been one of the major features of recent studies in adsorption (Gupta and Bhattacharyya, 2011). Kinetic study is important to an adsorption process because it depicts the uptake rate of adsorbate, and controls the residual time of the whole adsorption process (Demirbas *et al.,* 2009). Thus in order to find the appropriate kinetic model describing the adsorption of phenol onto activated

carbons prepared from *African beech* sawdust, four kinetic models namely; pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion were tried to fit the experimental data.

Lagergren first order model

The Lagergren first order kinetic processes signify reversible interactions with an equilibrium being established between liquid and solid phases (Low *et al.,* 2007).

The model is represented by: $\ln (q_e - q_t) = \ln q_e - K_1 t$ (Lagergren, 1898).

Where K_1 (1/min) is the pseudo first order adsorption rate coefficient, q_e and q_t are the values of amount adsorbed per unit mass at equilibrium and at any time t. The values of K_1 and the calculated q_e can be obtained respectively from the slope and intercept of the linear plot of $\ln (q_e - q_t)$ versus (t).

The values of K_1, calculated q_e values and correlation coefficients R^2 obtained from the plots for adsorption of phenol on the activated carbons prepared from *African beech* sawdust are given in Table 2 . The model's R^2 values were found to be relatively high > 0.95 and the experimental q_e values were found to be in good agreement with those calculated q_e values obtained from the linear Lagergren plots. Thus it can be concluded that the adsorption of phenol on *African beech* sawdust activated carbons follows the Lagergren first order kinetics and that the process depends on both the solution concentration and the number of available adsorption sites (Gupta and Bhattacharyya, 2011).
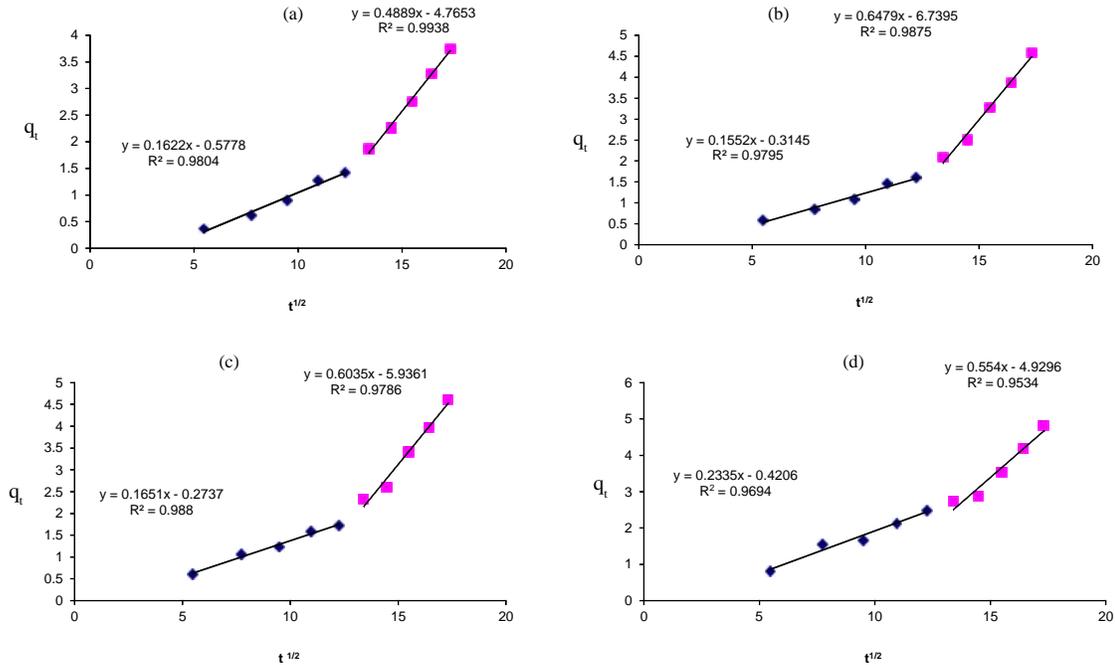
Fig. 5: Intraparticule diffusion mechanism for the adsorption of phenol onto (a) AC0, (b) AC1, (c) AC2 and (d) AC3

Table 2: The first-order, second-order and Elovich's kinetic models' constants for phenol adsorption by different activated carbons prepared from African beech sawdust.

	First-order kinetic model				Pseudo-second-order model				Elovich's model					q_e Experimental (mg/g)
	$K_{1,ad}$ 1/min	$q_{calc.}$ (mg/g)	R^2	q	$K_{2,ad}$ (g/mg.min)	$q_{calc.}$ (mg/g)	R^2	q	a (mg/g min)	b (g/mg)	$q_{calc.}$ (mg/g)	R^2	q	
AC0	0.0044	4.09	0.9547	0.35	4.36×10^{-4}	5.88	0.7895	2.14	36.3461	0.8574	4.01	0.8853	0.271	3.74
AC1	0.0035	4.64	0.9528	0.07	4.65×10^{-4}	6.03	0.5943	1.46	41.15015	0.7368	4.63	0.8664	0.060	4.57
AC2	0.0037	4.58	0.9583	0.02	6.37×10^{-4}	5.60	0.7368	1	36.5061	0.7441	4.43	0.8776	0.170	4.6
AC3	0.0051	4.75	0.9685	0.05	2.92×10^{-4}	9.22	0.6706	4.42	30.8512	0.7245	4.29	0.8582	0.510	4.8

Pseudo-second order model

The second order kinetic model assumes that the rate-limiting step is most likely to involve chemical interactions leading to binding of the ions to the surface by bonding as strong as covalent bonding (Gupta and Bhattacharyya, 2011).

The pseudo-second-order equation (Ho and McKay, 1998) based on equilibrium adsorption is expressed as: $t/q = 1/K_2 q_e^2 + t/q_e$; where K_2 (g/mg min.) is the rate constant of second-order adsorption. Plots of (t/q_t) versus (t) give $1/q_e$ as the slope and $1/K_2 q_e^2$ as the intercept.

The values of K_2 and correlation coefficient, R^2 obtained from the plots for adsorption of phenol on *African beech* sawdust activated carbons are given in

Table 2. The R^2 values were found to be relatively small ($R^2 < 0.8$) and the experimental q_e values did not agree with the calculated values obtained from the linear plots.

Elovich model

Elovich's equation assumes that the actual solid surfaces are energetically heterogeneous and that neither desorption nor interactions between the adsorbed species could substantially affect the kinetics of adsorption at low surface coverage (Gupta and Bhattacharyya, 2011). Elovich's equation is given as: $q_t = (1/b) \ln (ab) + (1/b) \ln (t)$; where a (mg/g.min) is the initial sorption rate and b (g/mg) is related to the extent of surface coverage and activation energy for chemisorption. The constants of the Elovich's equation

Table 3: Intraparticulediffsion mechanism constants for phenol adsorption by different activated carbons prepared from African beech sawdust

	Intraparticle diffusion					
	K_1 (mg/g min$^{-0.5}$)	$C_{b(1)}$ (mg/g)	R^2	K_2 (mg/g min$^{-0.5}$)	$C_{b(2)}$ (mg/g)	R^2
AC0	0.1622	0.5778	0.9804	0.4889	4.7653	0.9938
AC1	0.1552	0.3145	0.9795	0.6479	6.7395	0.9875
AC2	0.1651	0.2737	0.9880	0.6035	5.9361	0.9786
AC3	0.2335	0.4206	0.9694	0.554	4.9296	0.9534
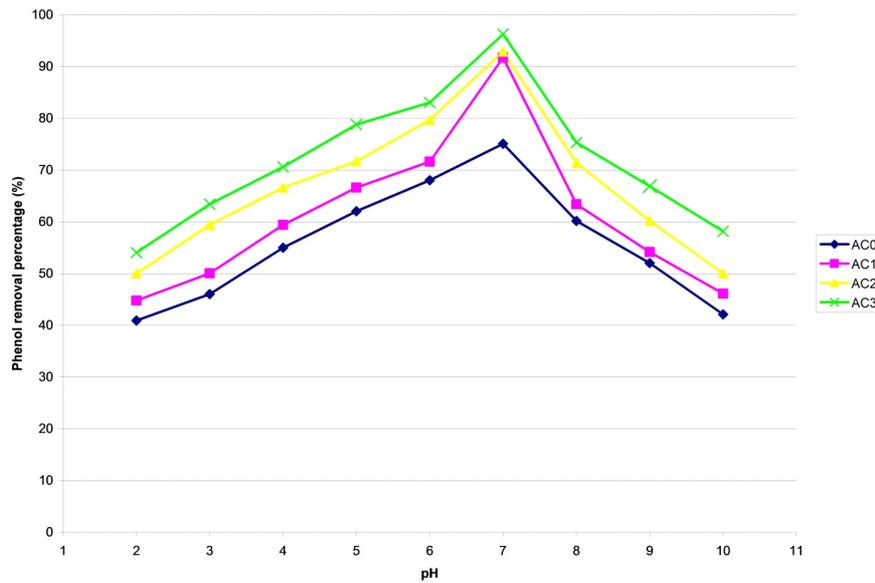
Fig. 6: Effect of solution pH on phenol removal by *African beech* wood sawdust activated carbons

for the same experimental data and given in Table 2 were obtained from the slope and intercept of the plots of$q_t$versus ln (t). The value of (1/b) is indicative of the number of sites available for adsorption while the (1/b) ln(ab) is the adsorption quantity when ln t is equal to zero; i.e., the adsorption quantity when t is 1 h (Tan *et al., 2009*).The R^2 values obtained from Elovich's equation were found to be relatively high ($R^2 > 0.85$) and the q_e values calculated from Elovich's equation agreed well with the experimental values.

Intra-particle diffusion

For porous adsorbents, the diffusion of the adsorbate molecules into the pores is also to be taken into account in finding a suitable kinetic model for the process. In many cases, the intra particle diffusion may control the rate of uptake of an adsorbate (Gupta and Bhattacharyya, 2011). The intraparticle diffusion equation, suggested by Weber and Morris (1963) can be expressed by: q_t=

$K_{(i)}$ $t^{0.5}$ + $C_{b(i)}$; where q_t is the adsorbed quantity of phenol, K_i is the intraparticle diffusion parameter, and $C_{b,i}$ is the thickness of the boundary layer at stage (i). The Plots (q_t) versus ($t^{0.5}$) representing the intraparticle diffusion model are given in Fig. 8. The parameters obtained from the intraparticle plots are listed in Table 3.

From Table 3 it can be observed that high correlation coefficient values ($R^2 > 0.95$) were obtained for the intraparticle diffusion model suggesting the applicability of the model for describing the adsorption of phenol onto activated carbons prepared from *African beech* sawdust.

As can be noticed from Fig. 5 multi-linear plots with two linear portions were obtained for the adsorption of phenol onto activated carbons prepared from *African beech* sawdust. According to El-Naas *et al. (*2010) the first linear portion of these plots represents the external diffusion by macropore and
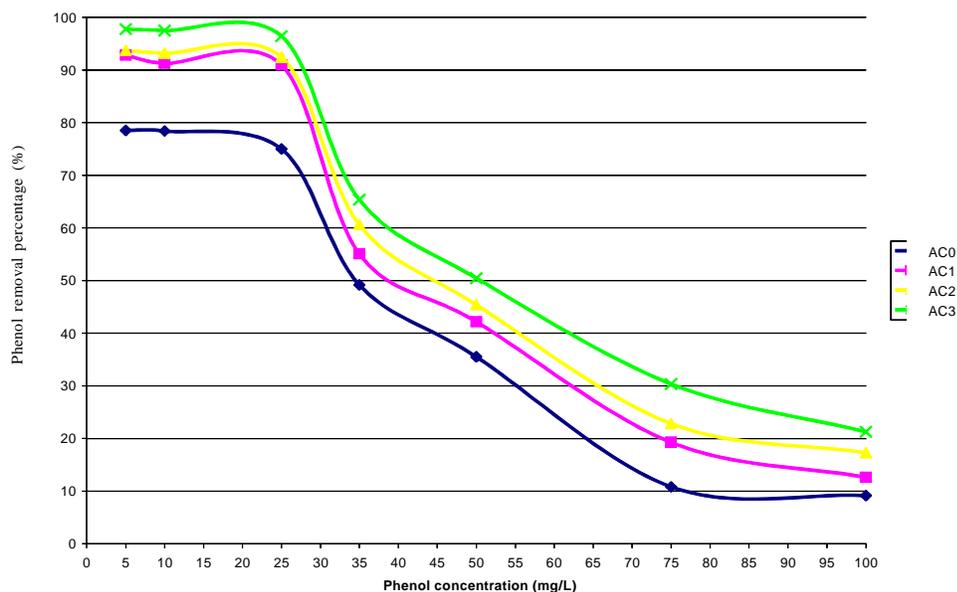
Fig. 7: Effect of initial phenol concentration on its removal by AC0, AC1, AC2 and AC3

mesopore; whereas the second portion of the plot indicates the micropore diffusion by the intraparticle diffusion (Aksu and Kabasakal, 2004). It has to be also noted that the plots did not pass through the origin indicating that the rate limiting process is not only due to the intraparticle diffusion some other mechanism along with intraparticle diffusion is also involved in the adsorption process (Tan *et al.,* 2009).

Effect of solution pH

Hydrogen ion concentration in the adsorption is considered to be one of the most important parameters that influence the adsorption behavior of phenol in aqueous solutions (Kilic *et al.,* 2011). The effect of solution pH on the removal of phenol by African beech sawdust activated carbons was studied over a pH range from 2 to 10 and the results are presented in Fig.6.

The experimental results showed that the maximum phenol removal percentages were obtained at around pH 7 and decreased on either sides of pH 7 for the different studied adsorbents. It is worth noting that phenol exists predominantly as neutral species at pH 7 (Nadavala *et al.,* 2009). The pH dependence of phenol adsorption can largely be related to the type and ionic state of the activated carbon surface functional groups and also on the phenol chemistry in solution (Beker *et al.,* 2010). Nadavala *et al.* (2009) explained the effect of solution pH on the removal of phenols and their

derivatives from aqueous solution by considering the presence of ionic and molecular forms of phenolic compounds in aqueous solution. These compounds act as weak acids in aqueous solution, and the dissociation of hydrogen ion from phenolic compounds strongly depends on the pH of the solution. In acidic solutions, the molecular form dominates and in alkaline medium, the anionic form is the predominant species.

It was suggested that the aromatic compounds adsorb on active carbon by a donor-acceptor complex mechanism involving carbonyl-oxygens of the carbon surface acting as the electron donor and the aromatic ring of the solute acting as the acceptor (Mattson *et al.,* 1969).The decrease in phenol adsorption at pH <7 can be explained by the increased H^+ adsorption on the carbonyl sites, which suppresses phenol adsorption on these sites. On the other hand, the decrease in the phenol amount adsorbed at pH>7 is attributed to both greater solubility of dissociated phenol at pH>pKa and increased repulsion forces between the dissociated form of the adsorbate and the carbon surface due to high concentration of OH⁻ (El-Naas *et al.,* 2010). In agreement with our results many researchers have found that pH around 7 was the optimum pH for phenol removal onto different types of activated carbons (Beker, 2010; El-Naas, 2010; Kilic *et al.,* 2011). Therefore, the optimum solution pH was selected to be 7 for our further adsorption experiments.

Table 4: Sorption isotherm coefficients of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) models applied to phenol adsorption by different activated carbons prepared from African beech sawdust

	Langmuir			Freundlich			Temkin			Dubinin-Radushkevich		
	$q_{max.}$ (mg/g)	b (L/mg)	R^2	K_F	n	R^2	a_T	b_T	R^2	q_s (mg/g)	B_D	R^2
AC0	1.732	0.252	0.961	1.035	2.335	0.777	1.103	0.841	0.777	3.469	6.00E-07	0.944
AC1	2.597	0.353	0.980	1.856	3.319	0.672	2.285	0.685	0.638	4.075	1.00E-07	0.923
AC2	3.447	0.867	0.980	2.012	3.236	0.672	2.488	0.749	0.699	4.458	1.00E-07	0.955
AC3	4.336	1.524	0.997	2.636	3.893	0.703	3.204	0.677	0.735	4.982	5.00E-08	0.979

Table 5: Langmuir isotherm separation parameter, R_L for phenol adsorption by different activated carbonsprepared from African beech sawdust

Initial phenol conc. (mg/L)	R_L			
	AC0	AC1	AC2	AC3
5	0.441	0.361	0.187	0.187
10	0.283	0.220	0.103	0.103
25	0.136	0.101	0.044	0.044
35	0.101	0.074	0.031	0.031
50	0.073	0.053	0.022	0.022
75	0.050	0.036	0.015	0.015
100	0.038	0.027	0.011	0.011

Effect of initial phenol concentration

Fig. 7 gives the effect of initial phenol concentration on its removal from aqueous solution by the four prepared activated carbons over a concentration range from 5 to 100 mg/L. It was observed that the removal of phenol was high at lower concentrations and decreased by increasing the phenol concentration. The higher phenol adsorption at lower concentrations may be due to the presence of more available sites on the adsorbent than the number of phenol ions which are available in the solution. However, at higher concentrations the number of phenol ions is relatively higher than available sites for adsorption (Kilic *et al.,* 2011). The maximum removal percentages were determined at 5 mg/L initial phenol concentration as 79, 93, 94 and 98% for AC0, AC1, AC2 and AC3; respectively.

Adsorption isothermal modeling

Equilibrium isotherms are fundamental in describing the interactive behavior between the solutes and adsorbent and also essential in the design of an adsorption system (Wan Ngah and Fatinathan, 2008). In the present study, four adsorption isotherms: the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D-R) isotherms were applied to ût the equilibrium data of adsorption of phenol on the *African beech* sawdust activated carbons. The Langmuir, (1916) model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the

plane of the surface. The linear form of the Langmuir equation is given by: $C_{eq}/q_e = 1/bq_{max} + C_{eq}/q_{max}$; where q_e (mg/g) is the amount of solute adsorbed per unit weight of adsorbent at equilibrium, C_{eq}(mg/L) the equilibrium concentration of the solute in the bulk solution, q_{max} (mg/g) is the maximum adsorption capacity, and b (l/mg)is the Langmuir constant related to the affinityof binding sites. The Langmuir adsorption isotherms of phenol on AC0, AC1, AC2 and AC3 were obtained by ploting C_e/q_e versus C_e. The empirical model proposed by Freundlich, (1906) is shown to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surfaces. The amount of sorbate adsorbed, q_e, is related to the concentration of sorbate in the solution through the following equation: $\log q_e = \log K_f + (1/n) \log C_{eq}$; where K_F and *n* are Freundlich constants. The experimental data of the present study were ûtted to the Freundlich equation and the parameters (K_f and n) were evaluated from the plots of log q vs. log C.

The Temkin, (1941) isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. Temkin model is given by: $q_{eq} = a_t + b_t \ln C_{eq}$; where b_t and a_t are Temkin isotherm constants obtained from the plots of Q against ln C.

The Dubinin–Radushkevich (D-R) isotherm (Dubinin, 1947), on the other hand, is based on the potential theory of adsorption for adsorbents with an energetically non-uniform surface where the dominant adsorption interaction is dispersion forces. The D–R model is used to determine if adsorption occurred by physical or chemical processes (Unlu and Ersoz, 2006) and it is presented mathematically as: $\ln q = \ln q_s - B_D \varepsilon^2$; where q_s is the theoretical isotherm saturation capacity, ε is the Polanyi potential and $B_D (mol^2/kJ^2)$ is constant related to the free energy of sorption per mole of sorbate as it migrates to the surface of the adsorbent from infinite distance in the solution (El-Naas *et al.,* 2010). The values of q_s and B_D were calculated from the intercept and slope of the $\ln q$ vs. ε^2 plots. The values for the determined parameters of each isotherm are shown in Table 4, together with the respective R^2 value for each model. Comparison of the obtained R^2 values shows that the experimental data fitted the isothermal models in the order: Langmuir> D-R>Freundlich and Temkin. The good fit of the experimental data with the Langmuir model may be attributed to the homogenous distribution of active sites on the surface of the prepared activated carbons. The favorable nature of adsorption can be expressed in terms of dimensionless Langmuir equilibrium parameter (Hall *et al.,* 1966): $R_L = 1/(1 + bC_i)$, where *b* is the Langmuir constant and C_i is the initial concentration of the adsorbate in solution. The values of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0<R_L<1$), linear ($R_L= 1$) or unfavorable ($R_L> 1$) (Abdel-Ghani *et al.,* 2009). As seen from Table 5 the R_L values for the different initial concentrations of phenol adsorbed onto AC0, AC1, AC2 and AC3; were found to lie between zero and one indicating favorable adsorption of phenol on the studied adsorbents.

The Langmuir maximum adsorption capacity values of the present study were compared to some previously investigated adsorbents. The maximum adsorption capacity of phenol by activated carbons prepared from coconut shells was 0.36 mmol/ g (Singh *et al.,* 2008). The maximum uptake of phenol by *Tectonagrandis* sawdust was found to be 2.82 mg/g (Mohanty *et al.,* 2005). Coke breeze showed a capacity of 0.18 mg/g for phenol removal whereas the adsorption capacity was found to be 4.5 mg/g for phenol removal by Rice husk (Ahmaruzzaman and Sharma, 2005).

CONCLUSION

In the present study, the preparation of activated carbon from *African beech* wood sawdust a locally available waste was successfully achieved. The surface characteristics of the produced carbons were highly affected by the weight ratio of KOH to char used in the activation process. The prepared activated carbons had high brunauer–emmett–teller (BET) surface areas ranging from 1236.8 to 1553.8 m^2/g. The surface morphology of the prepared adsorbents obtained from the SEM analysis revealed well developed pores. The adsorption process of phenol by the prepared activated carbons was optimized at a contact time of 300 min. and initial solution pH of 7. Kinetic studies showed that the adsorption of phenol onto *African beech* sawdust activated carbons followed the first –order kinetics model. The adsorption experimental data showed a good fit to the Langmuir and D-R isotherms.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

Abdel-Ghani, N.T.; Hegazy, A.K.; El-Chaghaby, G.A., (2009). Typha domingensis leaf powder for decontamination of aluminium, iron, zinc and lead: Biosorption kinetics and equilibrium modeling. Int. J. Environ. Sci. Technol. 6: 243-248 (**6 pages**). doi:10.1007/BF03327628

Adinata, D.; Daud W.M.A.W.; Aroua M.K., (2007). Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3. Bioresour. Tech. 98:145–149 (**5 pages**).

Ahmaruzzaman, M.; Sharma, D.K., (2005). Adsorption of phenols from wastewater. J. Colloid Interface Sci. 287:14–24 (**11 pages**). doi:10.1016/j.jcis.2005.01.075

Aksu, Z. ; Kabasakal E., (2004). Batch adsorption of 2,4-dichlorophenoxy-acetic acid (2,4- D) from aqueous solution by granular activated carbon. Sep. Purif. Technol. 35: 223-240 (**18 pages**). doi:10.1016/S1383-5866(03)00144-8

Aksu, Z.; Yener J., (2001). A comparative adsorption/biosorption study of monochlorinated phenols onto various sorbents. Waste Manag. 21:695-702 (**8 pages**).

Asadullah, M.; Asaduzzaman, M.; Kabir, M. S.; Mostofa, M. G.; Miyazawa, T., (2009). Chemical and structural evaluation of activated carbon prepared from jutesticks for Brilliant Green dye removal from aqueous solution. J. Hazard. Mater. 174:437-443 (**7 pages**).

Beker, U.; Ganbold, B.; Dertli, H.; Gülbayir, D.D., (2010). Adsorption of phenol by activated carbon: Influence of activation methods and solution pH. Energ. Convers. Manage. 51: 235–240 (**6 pages**). doi:10.1016/j.enconman.2009.08.035

Daifullah, A.A.M. ; Girgis, B.S., (1998). Removal of some substituted phenols by activated carbon obtained from agricultural waste. **Water Res.** 32: 1169–1177 (**9 pages**).

Demirbas, E.; Dizge, N.; Sulak, M.T.; Kobya, M., (2009). Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon, Chem. Eng. J., 148: 480–487(**8 pages**).

Dubinin, M.M.; Radushkevich, L.V., (1947). Equation of the characteristic curve of activated charcoal, Proceedings of the Academy of Sciences, Physical Chemistry Section, U.S.S.R., 55: 331-333 (**3 pages**).

El-Hendawy, A. A., (2009). An insight into the KOH activation mechanism through the production of microporous activated carbon for the removal of Pb^{2+} cations. Appl. Surf. Sci. 255: 3723–3730 (**8 pages**).doi:10.1016/j.apsusc.2008.10.034

El-Naas, M. H. ; Al-Zuhair S. ; Manal Abu Alhaija, (2010). Removal of phenol from petroleum refinery wastewater through adsorption on date-pit activated carbon. Chem. Eng. J. 162:997–1005 (**9 pages**). doi:10.1016/j.cej.2010.07.007

Freundlich, H.M.F., (1906), Uber die adsorption in losungen, *Zeitschrift* für Physikalische Chemie (Leipzig), 57A:385-470 (**6 pages**).

Galiatsatou, P. ; Metaxas, M. ; Kasseloui-Rigopoulou, V., (2001). Mesopores activated carbon from agricultural by products. Mikrochimica Acta. 136(3): 147-152 (**6 pages**).

Gupta S. S., Bhattacharyya K. G., (2011). Kinetics of adsorption of metal ions on inorganic materials: A review. Adv. Colloid. Interfac. 162: 39–58 (**10 pages**).

Hall, K.R.; Eagleton, L.C.; Acrivos, A. ; Vermeulen, T., (1966). Pore and solid diffusion kinetics in ûxed-bed adsorption under constant pattern conditions. Ind. Eng. Chem. Fund. 5: 212–223 (**2 pages**).

Hameed, B.H.; Daud, F.B.M., (2008). Adsorption studies of basic dye on activated carbon derived from agricultural waste: *Hevea brasiliensis* seed coat.Chem. Eng. J.139: 48–55 (**8 pages**).

Hameed, B.H.; Din, A.T.M.; Ahmadm, A.L., (2007). Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies. J. Hazard. Mater. 141: 819-825 (**7 pages**).

Hanafiah, M.A.; Ngah, W.S.; Zolkafly, S.H.; Teong, L.C.; Majid, Z.A., (2012). Acid Blue 25 adsorption on base treated Shorea dasyphylla sawdust: Kinetic, isotherm, thermodynamic and spectroscopic analysis. J. Environ. Sci. 24: 261–268 (**8 pages**).

Ho, Y.S.; McKay, G., (1998). The kinetics of sorption of basic dyes from aqueous solutions by sphagnum moss peat. Can. J. Chem. Eng. 76: 822–827 (**6 pages**).

Hu, Z.; Srinivasan, M.P., (1999). Preparation of high-surface-area activated carbons from coconut shell, Micropor. Mesopor. Mat. 27: 11–18 (**8 pages**).

Ioannidou, O.; Zabaniotou, A., (2007). Agricultural residues as precursors for activated carbon production: A review. Renew. Sustainable Energ. Rev.11: 1966–2005 (**10 pages**).

Jain, M.; Garg, V. K.; Kadirvelu, K., (2010). Adsorption of hexavalent chromium from aqueous medium onto carbonaceous adsorbents prepared from waste biomas. J. Environ. Manage. 91: 949–957 (**8 pages**).

Jibril, B. Y. ; Al-Maamari, R. S. ; Hegde, G. ; Al-Mandhary, N. ; Houache, O., (2007). Effects of feedstock pre-drying on carbonization of KOH-mixed bituminous coal in preparation of activated carbon. J. Anal. Appl. Pyrol. 80:277-282 (**6 pages**).

Juang, R.S.; Wu, F.C.; Tseng, R.L., (2002). Characterization and use of activated carbons prepared from bagasses for liquid-phase adsorption. Colloid. Surface A. 201:191–199 (**10 pages**).

Kalavathy, H. ; Karthik, B. ; Miranda, L. R., (2010). Removal and recovery of Ni and Zn from aqueous solution using activated carbon from Hevea brasiliensis: Batch and column studies. Colloid. Surface B. 78: 291–302 (**12 pages**).

Kalderis, D.; Bethanis, S.; Paraskeva, P.; Diamadopoulos, E., (2008). Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times, Bioresour. Tech. 99:6809–6816 (**18 pages**).

Karagozoglu, B. ; Tasdemir, M. ; Demirbas, E. ; Kobya, M., (2007). The adsorption of basic dye (Astrazon Blue FGRL) from aqueous solutions onto sepiolite, fly ash and apricot shell activated carbon: kinetic and equilibrium studies. J. Hazard. Mater. 147:297–306 (**10 pages**).

Kilic, M.; Apaydin-Varol, E.; Pütün, A. E., (2011). Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: Equilibrium, kinetics and thermodynamics. J. Hazard. Mater. 189:397–403 (**7 pages**).

Kumar, P. B.G.; Shivakamy, K.; Miranda, L. R.; Velan, M., (2006). Preparation of steam activated carbon from rubberwood sawdust (Hevea brasiliensis) and its adsorption kinetics. J. Hazard. Mater. 136: 922-929 (**8 pages**).

Lagergren, S., (1898). Kungliga Svenska Vetenskapsakademiens. Handlingar. 24:31-39 (**10 pages**).

Langmuir, I., (1916). The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38: 2221-2295 (**6 pages**).

Lin, S.H.; Cheng, Y.H.J., (1999). Adsorption of BTEX from aqueous solutions by macro reticular resins. J. Hazard. Mater. 70:21-37 (**7 pages**).

Ljupkoviæ, R.B.; Mitroviæ, J.; Radoviæ, M.; Kostiæ, M.; Bojiæ, D.; Mitiæ-Stojanoviæ, D-L.; Bojiæ, A.Lj., (2011). Removal Cu(II) ions from water using sulphuric acid treated *Lagenaria vulgaris* Shell. Biologica Nyssana**.**2: 85-89 (**5 pages**).

Low, K.S.; Lee, C.K.; Liew, S.C., (2007). Sorption of cadmium and lead from aqueous solutions by spent grain. Process Biochem. 36: 59-64 (**6 pages**).

Mattson, J.S.; Mark, Jr. H.B.; Malbin, M.D.; Weber, I.W.J.; Crittenden, J. C., (1969). Surface chemistry of active carbon: Specific adsorption of phenols, J. Colloid. Interf. Sci. 31: 116-130 (**15 pages**).

Mohanty, K.; Das, D.; Biswas, M.N., (2005). Adsorption of phenol from aqueous solutions using activated carbons prepared from Tectona grandis sawdust by $ZnCl_2$ activation. Chem. Eng. J. 115:121–131 (**11 pages**). doi:10.1016/j.cej.2005.09.016

Moreno-Castilla, C., (2004). Adsorption of organic molecules from aqueous solutions on carbon materials, Carbon, 42: 83-94 (**12 pages**).

Nadavala, S. K.; Swayampakula, K.; Boddu, V.M.; Abburim, K., (2009). Biosorption of phenol and o-chlorophenol from aqueous solutions onto chitosan–calcium alginate blended beads, J. Hazard. Mater.162:482–489 (**8 pages**).

Nagda, G. K.; Diwan, A. M.; Ghole, V. S., (2007). Potential of tendu leaf refuse for phenol removal in aqueous systems. Appl. Ecol. Environ. Res. 5: 1-9 (**9 pages**).

Naiya, T. K. ; Chowdhury, P. ; Kumar, B. A. ; Kumar, D. S., (2009). Saw dust and neem bark as low cost natural biosorbent for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions. Chem. Eng. J. 148: 68–79 (**12 pages**).

Onal, Y.; Akmil-Ba°ar, C.; Sarici-Ozdemir, C.; Erdoðan, S., (2007). Textural development of sugar beet bagasse activated with $ZnCl_2$. J. Hazard. Mater. 142:138–143 (**6 pages**).

Podkoscielny, P.; Dabrowski, A.; Marijuk, O.V., (2003). Heterogeneity of activated carbons in adsorption of phenol aqueous solutions. Appl. Surf. Sci. 205: 297-303 (**7 pages**).

Rengaraj, S.; Moon, S.H.; Sivabalan, R.; Arabindoo, B.; Murugesan, V., (2002). Removal of phenol from aqueous solution and resin manufacturing industry wastewater using an agricultural waste: rubber seed coat. J. Hazard. Mater. 89 :185-196 (**12 pages**).

Sabio, E.; González-Martýn, M.L.; Ramiro, A.; González, J.F.; Bruque, J.M.; Labajos-Broncano, L.; Encinar, J.M., (2001). Influence of regeneration temperature on the phenols adsorption on activated carbon. J. Colloid Interf. Sci. 242: 31- 35 (**5 pages**).

Seey, T.L.; Kassim M.J.N.M., (2012). Characterization of mangrove bark adsorbent and its application in the removal of textile dyes from aqueous solutions. J. Appl. Phytotechnol. Environ. Sanit. 1: 121-130 (**10 pages**).

Singh, K.P.; Malik, A.; Sinha, S., Ojha P., (2008). Liquid-phase adsorption of phenols using activated carbons derived from agricultural waste material. J. Hazard. Mater.150: 626–641 (**16 pages**).

Tan, I.A.W.; Hameed, B.H.; Ahmad, A.L., (2007). Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. Chem. Eng. J. 127: 111–119 (**10 pages**).

Tan, I.A.W.; Ahmad, A.L.; Hameed, B.H., (2008). Adsorption of basic dye on high surface area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies. J. Hazard. Mater. 154: 337-346 (**10 pages**).

Tan, I.A.W.; Ahmad, A.L.; Hameed, B.H., (2009). Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. J. Hazard. Mater. 164: 473-482 (**10 pages**).

Temkin, M.I., (1941). Adsorption equilibrium and the kinetics of processes on non homogeneous surfaces and in the interaction between adsorbed molecules, *Zhurnal* Fizicheskoi Khimii, 15: 296–332 (**7 pages**).

Thinakaran, N.; Baskaralingam, P.; Pulikesi, M.; Panneerselvam, P.; Sivanesan, S., (2008). Removal of Acid Violet 17 from aqueous solutions by adsorption onto activated carbon prepared from sunflower seed hull. J. Hazard. Mater. 151:316–322 (**7 pages**).

Tseng, R.L.; Tseng, S.K., (2005). Pore structure and adsorption performance of the KOH activated carbons prepared from corncob. J. Colloid Interf. Sci. 287: 428–437 (**10 pages**).

Unlu, N.; Ersoz, M., (2006), Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions. J. Hazard. Mater. B136: 272–280 (**9 pages**).

Wan Ngah, W.S.; Fatinathan, S., (2008). Adsorption of Cu(II) ions in aqueous solution using chitosan beads, chitosan– GLA beads and chitosan–alginate beads. Chem.Eng. J. 143: 62–72 (**11 pages**).

Weber, W.J.; Morris, J.C., (1963). Kinetics of adsorption on carbon from solutions, J. Sanit. Eng. Div. 89: 31–60 (**30 pages**).

Wu, F.C.; Tseng, R.L.; Juang, R. S., (2005). Preparation of highly microporous carbons from fir wood by KOH activation for adsorption of dyes and phenols from water. Sep. Purif. Tech. 47: 10-19 (**10 pages**).

Yan, J.; Quan, G. , (2009). Equilibrium and kinetic studies of phenol sorption by chitosan coated montmorillonite. J. Chil. Chem. Soc. 54: 73-76 (**4 pages**).

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