Research Article **Open Access**

Adsorption on Activated Carbon from Olive Stones: Kinetics and Equilibrium of Phenol Removal from Aqueous Solution

Thouraya Bohli[1]*, Nuria Fiol[2], Isabel Villaescusa[2] and Abdelmottaleb Ouederni[1]

[1]Laboratory of Research: Engineering Processes and Industrials Systems (LR11ES54), National School of Engineers of Gabes, University of Gabes, St Omar Ibn Elkhattab, 6029 Gabes, Tunisia
[2]Department d'Enginyeria Quimica, Agraria i Tecnologia Agroalimentaria,Universitat de Girona, Avda Lluis Santolo, 17003 Girona, Spain

Abstract

Activated carbon is prepared with chemical activation of olive stones, by using H_3PO_4. Batch adsorption of phenol from aqueous solution was investigated. The adsorptive properties were studied in terms of pH, equilibrium time, initial concentration (C_0: 25-300 mg/L) and particle sizes (0.125-1.6mm) effects. The experimental kinetic data fitted well the pseudo second order model and the equilibrium isotherm data the Langmuir model. The results indicate that chemical olive stones activated carbon is suitable to be used as an adsorbent material for adsorption of phenol from aqueous solution.

Keywords: Adsorption; Olive stones; Activated carbon; Phenol

Introduction

Phenol and its derivatives are toxic and carcinogenic in nature and are among the priority pollutants of the European Union and US Environmental Protection Agency [1]. Several methods, such as microbial degradation, adsorption, chemical oxidation, solvent extraction and reverse osmosis are being used for removing phenols from wastewater [2].

Activated carbons, the most important commercial adsorbents, are materials with large specific surface areas, high porosity, adequate pore size distributions and high mechanical strength [3,4]. Activated carbons can be produced from different carbonaceous materials such as coal, wood, peat and agricultural wastes especially lignocellulosic by-products. They are widely employed in water and wastewater treatment processes for removing organic compounds such as phenol and its derivatives [5,6].

Tunisia is classified in the fourth ranking of Mediterranean country in the production of olive oil. Therefore, olive trees cultivation constitutes a strategic position within the Tunisian agricultural sector, representing 1.6 million hectares under cultivation (30% of agricultural land area) and counting an estimated 60 million olive trees [7]. This high production implies a big quantity of olive stone waste. In a previous work [8], olive stones were used to prepare an activated carbon by chemical processes using H_3PO_4 (COSAC). This precursor is a by-product of oleic factories producing olive oil in Tunisian country. The produced activated carbon is characterized by a high surface area, developed micropores and heterogeneous functional groups.

The aim of this study was to investigate kinetics and equilibrium aspects of the adsorption of phenol onto olive stones activated carbon. Three kinetics models including pseudo-first order, pseudo-second order and intra-particle diffusion models were used to discuss adsorption mechanisms. Experimental equilibrium isotherms were fitted with Langmuir and Freundlich equations to analyze the adsorption process.

Materials and Experimental Methods

Activated carbon

Preparation: Activated carbon was prepared from olive stones by chemical activation with orthphosphoric acid (H_3PO_4) according to the method developed by Gharib et al. [8]. Initially, the precursor was washed thoroughly with water, dried and then impregnated with a dilute phosphoric acid solution for 9 hours at 110°C. The resulting materials were washed with distilled water to remove any leachable impurities. The dried solid was carbonized in a vertical tubular fixed bed reactor heated at controlled temperature by electric furnace and fed with a continuous nitrogen flow. The carbonization time and temperature were optimized to be 2 h 30 min and 410°C respectively. The producer of carbon was washed with distilled water and then dried to be ready for using.

Characterization of the activated carbon:

a. Specific surface area and textural proprieties: Specific surface area and pores characteristics of activated carbon were determined by nitrogen adsorption and desorption isotherms at 77.7 K with an automatic Sorptiometer Autosorbe-1C Quantachrome apparatus (Common Services Research Unit of ENIG). The activated carbon sample is previously out gassed at 250°C and under vacuum. The micropores volume is estimated from nitrogen isotherm by analyzing the nitrogen adsorption isotherm at 77 K by Dubinin and Radushkevich micropore analysis method. The total pore volume is estimated from the adsorption quantity of nitrogen at relative pressure near unity. The measured values of textural characteristics are reported in Table1, we note the important micropore volume and a high specific surface area.

b. Determination of pH_{pzc}: The point of zero charge (pHPZC), pH at which the adsorbent is neutral in aqueous suspension, was determined following the procedure of Lopez-Ramon [9]. In this method 50 ml of 0.01M NaCl solutions were filled in closed Erlenmeyer

PARAMETERS	VALUE
Apparent specific weight (g/cm³)	0.55
Specific surface area BET (m²/g)	1040
Micropores volume (cm³/g)	0.463
Mesopores volume (cm³/g)	0.014
Total pore volume (cm³/g)	0.477
Average pores diameter (nm)	1.835
pH_{pzc}	3.00

Table 1: Physical and chemical characteristic of olive stones activated carbon.

flasks under agitation at room temperature of about 25°C. The pH of each solution is initially fixed at value lying from 2 to 12 by adding 0.1M HCl or 0.1M NaOH solutions. Then 0.1g of solid adsorbent was added to each flask and the final pH was measured after 48 h. pH_{PZC} is localized at the point where the curve pH_{final} versus $pH_{initial}$ intersects the first bisector. The fined value is pHpzc=3, showing that the activated carbon is anionic.

Phenol

Analytical-reagent grade phenol (purity>99%), was used as the adsorbate. A stock solution was prepared by dissolving required amount of phenol in double distilled water. Different initial concentrations (C_0) of phenol, in the range of 25-300 mg/l, were obtained by successive dilutions.

Phenol concentration was determined by UV absorption at 270 nm wave-length using a calibrated UV-Visible spectrophotometer.

Isotherm equilibrium adsorption construction

Experiments were carried out by dispersing known quantities of adsorbent (0.1- 0.5 g) within 200 ml of 400 mg/l phenol solution in 250 ml flasks. Adsorption equilibrium isotherms were measured via batch mode adsorption technique by placing volumetric flasks in a shaking mixer and using a thermostatic bath to control and to fix the temperature at 40°C. After 48 h of mixing at fixed instant speed of 500 rpm, samples were taken out from each flask and filtered. Initial and residual concentrations of phenol were measured using previously calibrated UV absorption at 270 nm analytical method.

For pH effect experimental study, the adsorption of phenol by COSAC was investigated over a pH range of 2 to 9 at 40°C with an initial solute concentration of 100 mg/l and an adsorbent carbon dose of 0.1 g. Experiments were carried out for 48 h at constant agitation speed of 500 rpm. Initial solution pH was adjusted by adding a diluted 0.1 M HCl or 0.1 M NaOH.

Kinetics adsorption

Kinetic adsorption was studied at various initial phenol concentrations (25-300 mg/l) and for different activated carbon particle sizes (0.125-1.600 mm) and the same quantity: 1.6 g in batch mixed suspension with 800 ml of phenol solution at given initial concentration. The temperature of the suspension was maintained constant at 40 °C by using a thermostatic bath. Samples of 5 ml were withdrawn at regular times and the residual phenol in the filtrates was measured.

The amount of phenol adsorbed on activated carbon q_t (mg/l) was followed versus time and was calculated using the following equation:

$$q_t = \frac{(C_O - C_t)V}{m}, \text{ (mg/g)} \tag{1}$$

Where C_0 and C_t are the concentration of phenol solution (mg/l) at initial and at sampling time (t) respectively; V the volume of solution

(l) and m is the weight (mg) of activated carbon. Each experiment was carried out in duplicated way and the average results are presented in this work.

Results and Discussion

Effect of initial pH on the adsorption

The pH of solution is one of the most important parameter affecting phenol adsorption processes because it affects the surface charge of the adsorbent as well as the degree of ionization and speciation of phenol [10]. Effect of initial pH on adsorption of phenol was studied with initial concentration of 100 mg/l and optimum carbon dose of 1 g/l and at a temperature of 40°C. Figure 1 shows the influence of solution pH on phenol removal by COSAC in the pH range of 2.0 to 9.0. The phenol adsorption decreases slowly with the increase of pH for values up than pH=4.0 and the adsorption sharply decreases for pH>6. The maximum phenol uptake obtained at pH lower than pHpzc (pHpzc=3) can be explained by the fact that at this pH range the COSAC surface is charged positively and phenol was protonated [11] this create a strong electrostatic interaction between phenol molecule carbon surface. However, with the increase of pH solution behind pHpzc, phenol become more and more dissociated and COSAC surface is charged more negatively leading to increased electrostatic repulsion force between the anionic phenol form and OH- groups on COSAC surface and between phenolate-phenolate anions in solution [12] resulting in a decrease of phenol uptake. Taking into account the obtained results further experiments were carried out at pH 2.3 without adjustment.
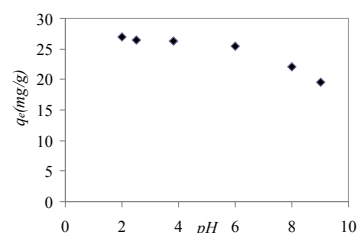

Figure 1: Effect of pH on the uptake of phenol onto COSAC (Temperature 313 K, initial concentration100 mg/l).
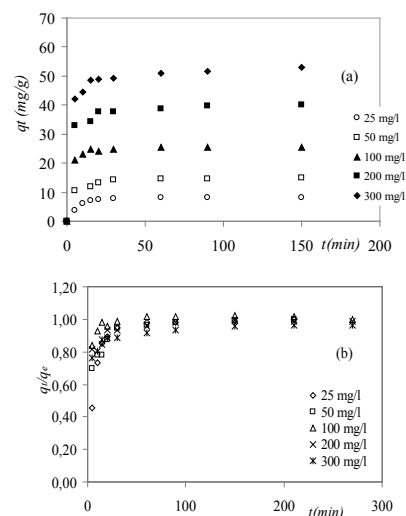

Figure 2: Initial concentration effect on process kinetics for the adsorption of phenol onto COSAC (Particle sizes: 0.630-1.000 mm, temperature 313 K, initial pH: 2.3).

Effect of contact time and initial concentration

Initial concentration effect on the removal of phenol is reported in Figure 2a. When initial phenol concentration increased from 25 to 300 mg/l, the adsorption capacity of COSAC increased from 8 to 53 mg/g. The time evolution of the amount adsorbed phenol indicates that the equilibrium time was reached at about 60 min for all the initial concentrations (Figure 2b). We observe two kinetics regions: the first one is characterized by a high adsorption rate and this is due to that initially the number of sites of activated carbon available is higher and the driving force for the mass transfer is greater. Therefore, phenol reaches the adsorption site easily. As time progress the number of free site of COSAC decreases and the non adsorbate molecules are assembled at the surface thus limiting the capacity of adsorption. The increase of loading capacities of COSAC with increasing phenol concentration may be due to higher π-π interaction between phenol and the surface function of activated carbon. π-π interaction is usually the mean involved mechanism of phenol adsorption [13,14].

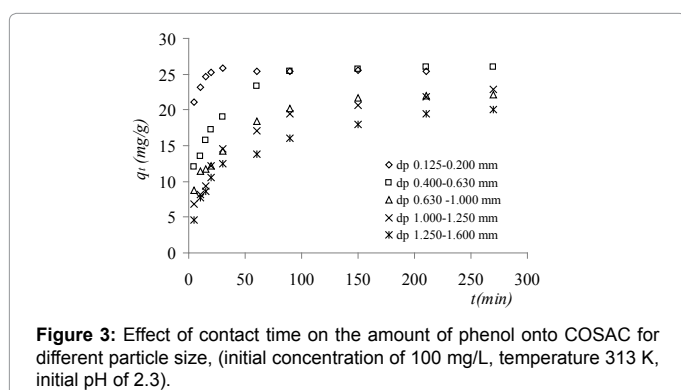## Effect of the particle size on the adsorption kinetic of phenol

The amount adsorbed phenol extent versus the agitation time for different particles sizes (0.125 - 1.6 mm) at the same phenol initial concentration of 100 mg/l, natural pH (around 2.3) and an stirrer speed of 500 rpm are shown in Figure 3. This high mixing speed was considered to be sufficient to overcome the external film diffusion resistance. Results show that: the smaller the particle size, the faster was the adsorption kinetic. We can also observe, for all particle sizes, that the adsorption processes could be subdivided in two steps: rapid first one followed by a slow step, this is become evident for small particle size. By else, with increasing particle size the phenol adsorption quantity decreases and the kinetic is slower. This confirms the hinting effect of the internal mass transfer process in the dynamic of the adsorption process.

Figure 3 suggests that there are two linear sections in each plot. The first section corresponds to the diffusion in the micropores. At the beginning of the phenol diffusion into COSAC, there is a fast initial uptake (part 1) with high intraparticle diffusion rate constant. It accounts for approximately 91% of the overall adsorption capacity for a particle size between 0.63 and 1 mm.

The first rapid step is due to a high interaction between adsorbent surface and phenol (sites with high affinity). The second step is relative to a less energetic adsorption with carbon sites having low affinity and formation of multilayer.

Adsorption kinetics

Pseudo-first-order, pseudo-second-order and intra particular

Figure 3: Effect of contact time on the amount of phenol onto COSAC for different particle size, (initial concentration of 100 mg/L, temperature 313 K, initial pH of 2.3).

diffusion models are applied to describe the kinetic data. The effect of initial concentration and particle sizes was investigated to find the best kinetic model.

Pseudo-first order model: The pseudo-first-order of Lagergren [15] is expressed in a linear form:

$$Ln(q_e - q_t) = k_1 t + Ln q_e \qquad (2)$$

Where k_1 is the rate constant of pseudo-first order adsorption (mn^{-1}), q_t and q_e are respectively the instantaneous and equilibrium amount of phenol adsorption per unit weight of activated carbon (mg/g) and t is the time (min). The plot of Ln $(q_e - q_t)$ versus t should give a linear relationship with the slope equal to: k_1.

Results given in Table 2 indicate that first order kinetic model does not correctly fit the experimental data for different initial concentration and particle sizes; coefficients regression are between 0.598 and 0.920 and the phenol uptakes are less then these given by experiment.

Pseudo-second order model: The kinetic data are fitted with pseudo-second order model resulting in the following linear equation [16]:

$$\frac{t}{q} = \frac{1}{K_2 q_e} + \frac{1}{q_e} t \qquad (3)$$

Where K_2 is the rate constant of pseudo-second order.

The linear plots of t/q_t versus t show that the experimental data agree with the pseudo-second order kinetic model. The calculated q_e (mg/g) (Table 2) values agree very well with the experimental data and the correlation coefficients close to the unit in all cases. These indicate that the adsorption of phenol from aqueous solution on COSAC obey the pseudo-second order kinetic model. It was observed also that the constant kinetic, k_2, decreased with the increasing of the initial phenol concentration and particles size. This shows the importance of transport process, particularly the internal diffusion in overall adsorption process kinetics some observations are reported by Srihari et al. [16].

Intra-particle diffusion: Intra-particle diffusion was often considered as the limiting step which limits the kinetics in the most process of adsorption. The possibility of a limitation by the diffusion in the pores is explored by plotting phenol uptake against the square root of time, using the Weber and Morris model:

$$q_t = k_d \sqrt{t} + C \qquad (4)$$

Where q_t is the instantaneous amount of phenol adsorption per unit gram of activated carbon (mg/g), C (mg/g) is a constant giving an idea about the thickness of the boundary layer: the larger the value of C is more important the lay effect limitation.

The intraparticle diffusion model plots for the adsorption of phenol onto COSAC, under the effect of initial phenol concentration and carbon particle size, suggest that there are two linear parts in each plot. The initial parts are attributed to boundary layer diffusion effects or external mass transfer effects. These lines do not pass through the origin indicating that the intra-particle diffusion is not the only process that can control kinetics of adsorption [16,17]. Whereas, the second parts may be attribute to intra-particle diffusion effects.

The rate constants: k_{d1} and k_{d2}, of intraparticle diffusion (mg/g), was calculated respectively from the slope of the first and second linear portion of the plots. It is obvious from Table 2 that k_{d1} is higher than K_{d2}. This can be related to the fact that firstly the number of pores available are very high and after there is possibility of pore blockage

or steric hindrance exerted by the adsorbed molecules on the carbon surface, it will eventually slow down the adsorption process and give rise to other linear sections with smaller intraparticle rate constants.

The validity of the order of adsorption processes is based on the regression coefficients and on predicted q_e values. Table 2 shows that correlation coefficients of the pseudo-second order kinetic model are the highest as compared to these given by the pseudo-first order and interparticle diffusion model. Either the q_e (mg/g) calculated by the pseudo-second order, agree very well with the experimental data. Thus indicate that the adsorption of phenol from aqueous solution on COSAC obey the pseudo-second order kinetic model.

Isotherm of adsorption

The adsorption isotherm of phenol on COSAC was studied at 30°C and an initial solution pH of 2.3. As can be seen from Figure 4 [18] and according to the classification of Brunauer, Emett, and Teller the adsorption isotherm of phenol on CACOS is of type IV shows the formation of two successive layers of phenol on the surface of activated carbon when the interactions between the molecules of phenol and the surface of adsorbent are stronger than the interactions between the adsorbed molecules. In this case, the sites of adsorption of the second layer begin to fill perform only when the first layer is complete.

The same shape of isotherm was found by Calace et al. [19], when they study the adsorption 4-nitrophenol (4-NP) on papermill sludges.

The first part of the equilibrium experimental isotherm was modeled by Langmuir and Freundlich equations (Figure 5). According to the theory of adsorption, the model of Langmuir is based on the fixation of a monolayer of adsorbate molecules on the surface of pores. The model assumes uniform adsorption on the surface and no transmigration in the plane of the surface. Langmuir's equation is mathematical expressed as follows.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (5)$$

Where: K_L is the equilibrium adsorption constant related to the free energy of the adsorption (l/mg) and q_{max}: the maximum adsorption capacity (mg/g), C_e the equilibrium concentration (mg/l), is the q_e

amount adsorbed at equilibrium (mg/g). The linear form of equation (5) is given equation (6):

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{max} K_L}\right) + \left(\frac{1}{q_{max}}\right) C_e \qquad (6)$$

The essential characteristics of Langmuir model can be expressed by dimensionless constant called separation factor, R_L, with is given by this equation:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (7)$$

The adsorption is considered as irreversible $R_L=0$, favourable when $0<R_L<1$, linear when $R_L=1$ and unfavourable when $R_L>1$.

The Freundlich equation is an empirical model that considers heterogeneous adsorptive energies on the adsorbent surface [15].

$$q_e = K_F C^{1/n} \qquad (8)$$

The linear form of equation (8) is given equation (9):

$$Log q_e = Log K_F + \frac{1}{n} Log C_e \qquad (9)$$

Where, K_F (l/g) and $1/n$ are Freundlich constants. The parameters of both models are calculated and summarized in Table 3.

Figure 5 shows that Langmuir equation is more reasonably applicable than Freundlich equation with correlation coefficients R^2 equal to 0.99 and an R_L of 0.061 indicating favourable adsorption of phenol on COSAC.

Ozkaya [20] studied the removal of phenol using a commercial activated carbon, Langmuir adsorption model give a maximum uptake of 49.7 mg/g. Srivastava et al. [15], were studied the adsorptive removal of phenol by bagasse fly ash (BFA) and two activated carbons ACC and ACL, maximums amount given by Langmuir model are respectively 23.83, 30.22 and 24.65 mg/g. Kilic et al. [21], investigated phenol adsorption from aqueous solutions by activated carbon prepared from tobacco residues, results show that maximums removal are 17.83 and 0.55 mg/g respectively for ACK1 and ACK2. In the present work, Table 2 shows a maximum uptake related to the first part of phenol isotherm of 58.82 mg/g and Figure 2 give an experimental value of the amount

	First order k_1(min⁻¹) q_e (mg/g) R²			second order k_2(min⁻¹) q_e R²			intra-particle diffusion k_{d1}(mg/g) R² kd_2(mg/g) R²			
Initial concentration (mg/L)										
25	0.0627	4.525	0.889	1.9847	25.575	1	1.6359	0.936	0.0675	0.7864
50	0.0544	9.387	0.734	0.1045	27.100	0.999	1.1192	0.929	0.0937	0.9512
100	0.1743	13.538	0.784	0.0698	23.419	0.998	1.4511	0.813	0.0194	α
200	0.0423	13.279	0.641	0.0493	24.038	0.998	1.8901	0.747	0.1822	0.7535
300	0.0384	15.825	0.598	0.0468	21.276	0.997	3.2479	0.952	0.3152	0.8573
Particle size (mm)										
0.125-0.2	0.1401	10.479	0.814	0.2104	8.803	0.996	1.464	0.915	0.0426	α
0.4-0.63	0.0341	18.541	0.935	0.3257	15.240	0.999	2.091	0.992	0.2557	α
0.63-1	0.0253	16.629	0.920	0.5509	25.773	1	1.535	0.926	0.4246	0.867
1-1.25	0.0226	17.101	0.923	0.5560	40.322	0.999	2.481	0.961	0.0613	0.957
1.25-1.6	0.0275	17.995	0.920	0.6428	52.631	1	2.386	0.984	0.7051	0.960

α: for values less than 0.7

Table 2: Kinetic parameters for the adsorption of phenol onto COSAC.

Langmuir parameters				Freundlich parameters		
q_{max} (mg/g)	K_L (l/mg)	R_L	R²	K_F (L/g)	n	R²
58.823	0.038	0.061	0.99	3.935	1.865	0.964

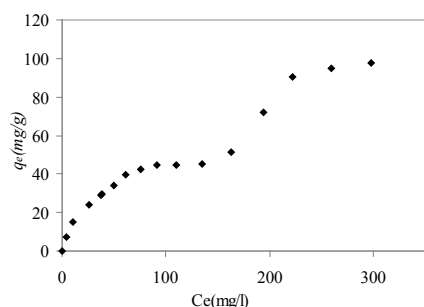**Table 3:** Langmuir and Freundlich sorption parameters.

Figure 4: Experimental adsorption isotherms of phenol onto COSAC (temperature: 313K, initial pH: 2.3, particle size: 0.630 -1.000 mm).
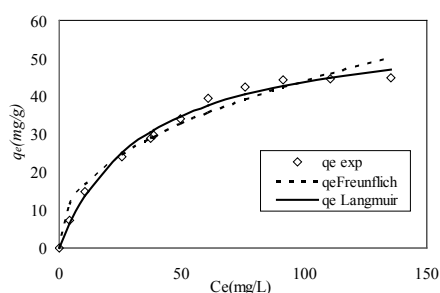

Figure 5: Comparison of experimental and predicted adsorption isotherms of phenol onto COSAC according to Langmuir and Freundlich models for the first part (temperature 313K, initial pH 2.3, particle size: 0.630-1.000 mm).

uptake related to the second part of this isotherm of about 97.6 mg/g. These results indicate that COSAC can be consider as a good adsorbent of phenol as compared by other materials for removing phenol, COSAC shows a high capacity to sorbs this pollute from water.

Conclusion

In this study, the adsorption of phenol from aqueous solution using olive stones activated carbon (COSAC) was investigated. Results indicate that adsorption capacity of COSAC was considerably affected by pH, initial concentration, and particle size. Phenol adsorbent increased with increasing initial concentration and decrease with the increase of particle size of activated carbon.

Kinetic experiments carried out with different particle sizes of COSAC showed that the smaller the particle size, the faster was the diffusion of phenol into adsorption sites of adsorbent. Kinetics results of phenol adsorption were examined using the pseudo-first-order, pseudo-second-order and intra particular diffusion kinetics models. The results obtained show that the pseudo-second order model was the best to describe adsorption kinetic data for phenol. Equilibrium data were fitted to Langmuir and Freundlich isotherms and the best fit was given by the Langmuir isotherm model, with a maximum monolayer adsorption capacity of about 58.8 mg/g. thus indicates that COSAC is suitable to be used as an adsorbent material for adsorption of phenol from aqueous solution it may also be effective in removing other harmful species such as heavy metals.

References

1. Santana CM, Ferrera ZS, Torres Padrón ME, Santana Rodríguez JJ (2009) Methodologies for the Extraction of Phenolic Compounds from Environmental Samples: New Approaches. Molecules 14: 298-320.

2. Liu QS, Zheng T, Wang P, Jiang JP, Liu N (2010) Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers. Chemical Engineering Journal 157: 348-356.

3. Ugurlu M, Gurses A, Acikyildiz M (2008) Comparison of textile dyeing effluent adsorption on commercial activated carbon and activated carbon prepared from olive stones by ZnCl2 activation. Microporous and Mesoporous Materials 111: 228-235.

4. Mohanty K, Das D, Biswas MN (2005) Adsorption of phenol from aqueous solutions using activated carbons prepared from Tectona grandis sawdust by ZnCl2 activation. Chemical Engineering Journal 115: 121-131.

5. Baudu M, Guibaud G, Raveau D, Lafrance P (2001) Prediction of adsorption from aqueous phase of organic molecules as a function of some physicochemical characteristics of activated carbons. Water Quality Research Journal of Canada 36: 631-657.

6. Ania CO, Parra JB, Pis JJ (2008) Effect of texture and surface chemistry on adsorptive capacities of activated carbons from phenolic compounds removal. Fuel Processing Technology 78: 337-343.

7. Hannachi H, Msallem M, Elhadj SB, El Gazzah M (2007) Influence du site géographique sur les potentialités agronomiques et technologiques de l'olivier (Olea europaea L.) en Tunisie. Comptes Renduus Biologies 330: 135-142.

8. Ouederni A, Gharib H (2005) Processing olive pomace Tunisian activated carbon chemically with phosphoric acid. Recent Advances in Process Engineering, SFGP, Paris, France.

9. Lopez-Ramon MV, Stoeckli F, Moreno-Castilla C, Carrasco-Marin F (1999) On the characterization of acidic and basic surface sites on carbons by various techniques. Carbon 37: 1215-1221.

10. Maleki A, Mahvi AH, Ebrahimi R, Khan J (2010) Evolution of Barley straw and its Ash in Removal of Phenol from Aqueous System. Word Applied Sciences Journal 8: 369-373.

11. Lü G, Hao J, Liu L, Ma H, Fang Q, et al. (2011) The Adsorption of Phenol by Lignite Activated Carbon. Chinese Journal of Chemical Engineering 19: 380-385.

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

13. Li D, Wu Y, Feng L, Zhang L (2012) Surface properties of SAC and its adsorption mechanisms for phenol and nitrobenzene. Bioresource Technology 113: 121-126.

14. Li Y, Du Q, Liu T, Peng X, Wang J, et al. (2013) Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes. Chemical Engineering Research and Design 91: 361-368. 15.

15. Srivastava VC, Swamy MM, Mall ID, Prasad B, Mishra IM (2006) Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics. Colloids and Surfaces A: Physicochemical Engineering Aspects 272: 89-104.

16. Srihari V, Das A (2008) The kinetic and thermodynamic studies of phenol-sorption onto three agro-based carbons. Desalination 255: 220-234.

17. Hall KR, Eagleton LC, Acrivos A, Vermeulen T (1996) Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. Industrial & Engineering Chemistry Fundamentals 5: 212-223.

18. Khalfaoui M, Knani S, Hachicha MA, Ben Lamine A (2003) New theoretical expressions for the five adsorption type isotherms classified by BET based on statistical physics treatment. J Colloid Interface Sci 263: 350-356.

19. Calace N, Nardi E, Petronio BM, Pietroletti M (2002) Adsorption of phenols by papermill sludges. Environmental Pollution 118: 315-319.

20. Ozkaya B (2006) Adsorption and desorption of phenol on activated carbon and a comparison of isotherm models. Journal of Hazardous Materials 129: 158-163.

21. Kilic M, Apaydin-Varol E, Pütün AE (2011) Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: Equilibrium, kinetics and thermodynamics. Journal of Hazardous Materials 189: 397-403.