

## دراسة حركية امتزاز بروتوكاتيكويك أسيد من المحاليل المائية على الفحم الفعال المشتق من النبات

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### □ ملخص □

درس امتزاز حمض البرتوكاتيكويك (مركب فينولي) من محاليله المائية على الفحم الفعال المشتق من النبات. درس الامتزاز بتغير الحجم الحبيبي للفحم الفعال وتغير التركيز الابتدائي للمركب الفينولي، حيث حطم الفحم وفصل إلى أربع حجوم حبيبية A,B,C,D، واستخدمت خمس تراكيز ابتدائية للمركب الفينولي وهي (10,20,30,40,50 ppm). بينت إيزوثرمات (متساويات درجة الحرارة) الامتزاز أن الامتزاز يتبع نموذجي لانغموير وفريندليتش. كانت سعة الامتزاز العظمى للفحم 0.36 mmol/g للحجم الحبيبي A. واعم قانون بسيدو الثاني نتائج الامتزاز أكثر منه لبسيدو الأول. كانت معادلة إلفينتش صالحة من أجل الحجمين الحبيين C,D عند كل التراكيز الابتدائية حيث كان معيار الصلاحية أقل من 10 لهذين الحجمين الحبيين. اختلف معامل انتشار المركب الفينولي باختلاف الحجوم الحبيبية للفحم وفق الترتيب التالي  $D(A) > D(B) > D(C) > D(D)$ .

الكلمات المفتاحية: امتزاز، الفحم الفعال، حمض البرتوكاتيكويك.

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## Adsorption Kinetics of Protocatechuic Acid From Aqueous solutions onto Activated Carbon Derived From Charcoal

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### □ ABSTRACT □

Commercial activated carbon derived from charcoal was used as an adsorbent to remove protocatechuic acid from its aqueous solution. Activated carbon was crashed and separated into four granular sizes A,B,C ,and D. Five initial concentrations of protocatechuic acid(10,20,30,40,50 ppm) were used to investigate the effect of initial concentration of pollutant on the adsorption on activated carbon. Adsorption isotherm studies indicated that activated carbon satisfy Langmuir and Freundlich models. The maximum adsorption capacity was found to be 0.36 mmol/g for granular size A. Pseudo second order fitted the adsorption. The Elovitch equation was valid for the granular size of activated carbon C,D at all initial concentrations of protocatechuic acid as the validity standard was less than 10. The values of diffusivity constants D are different according to the granular sizes of the adsorbent (A, B, C, D) as following : $D(A) > D(B) > D(C) > D(D)$ .

**Key words:** adsorption, activated carbon, protocatechuic acid.

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## Introduction

The phenolic compounds are one of the most important pollutants which affect the environment because they are non-biodegradable and toxic to microorganisms. Phenolic compounds exist in different industrial wastes like paper (Davis, and Burns 1992), petrochemical, textile, leather and coal industries (El-Naas et al., 2010; Kulkarni et al., 2013; Abdelkreem, 2013). Not to mention their existence in the waste of food industries like fruit industry and olive oil production (olive mill waste water (OMWW) (Hea et al., 2012; Heninia et al., 2012; Demarco et al., 2007).

Olive mill wastewater produced from olive oil production contains large quantities of phenolic compounds which cause its dark colour and damage the organisms. Many studies are revolved around the removal of phenolic compounds by using different techniques such as microbial degradation (Barbeau et al., 1997), chemical oxidation (Leyva et al., 1998), photocatalytic degradation using TiO<sub>2</sub> (Agrios and Gray 2003), sun photochemical (Shirgaonkar, 1998), ultrasonic degradation (Pandit and Gogate 2001), enzymatic polymerization (Buchanan, 1997), and adsorption (Burleigh et al., 2002). Among these, adsorption offers an efficient and economically feasible technology for the removal of contaminants from wastewaters. Selective adsorption utilizing biological materials, mineral oxides, and activated carbon or polymer resins has developed great interest among researchers and environmentalists. Activated carbon has been utilized as an efficient sorbent for odour removal, solvent recovery, decolourization, dechlorination, ozone annihilation, H<sub>2</sub>S/CS<sub>2</sub> removal, gold recovery, filtration, condensed devilling, fuel gas cleaning, industrial wastewater treatment, drinking water conditioning, etc. (Kunwar et al., 2007).

Activated carbons can be prepared from a variety of materials. The most commonly used raw materials for the preparation of activated carbons in commercial practice are peat, coal, lignite, wood and agricultural by-products. Production of activated carbon from agricultural by-products serves a double purpose by converting unwanted surplus agricultural waste to useful valuable material and providing an efficient adsorbent material for the removal of organic pollutants from water/waste water (Kunwar et al., 2007)

It is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate sorption treatment plants. Therefore, the kinetics that describes the pollutant uptake rate needs to be determined. The adsorption mechanism can be described by three steps:

1. External mass transfer from bulk solution to adsorbent surface across the boundary layer surrounding the adsorbent particle. This is basically determined by the hydrodynamic conditions; i.e., an increase in the agitation speed of the batch adsorber creates more turbulence and a decrease of boundary layer thickness around the particles.
2. Intraparticle diffusion within the internal structure of the particle. Internal diffusion is the diffusion of molecules inside the pores and surface diffusion is the diffusion of molecules on the surface phase. It controls the transfer of adsorbate from the exterior of the porous adsorbent to the internal surface site.
3. Adsorption at an interior site. This is the step where the particle is attached to the surface of the adsorbent. Adsorption at an interior site is usually considered to be very rapid and is neglected. (Thomas et al., 2006)

The surface characteristics and the porous structure of the activated carbon are the most important factors, which define the adsorptive behaviour of activated carbon for phenolic compounds (Radovic and Moreno, 2001; Moreno, 2004)

This research aimed to evaluate the efficiency of one the commercial activated carbons in term of phenolic compounds removal from olive mill waste water. The kinetic of adsorption of protocatechuic acid, which considering present in olive oil waste water, was studied using different models to characterize the adsorption process.

## Materials and methods

The commercial activated carbon named charcoal, which was used as adsorbent, was purchased from POCH (Polonia), table (1) shows the physicals specifications of the used charcoal activated carbon.

**Table (1): The properties of charcoal activated carbon.**

Particle diameter(mm)	0.2-0.6
Pore diameter (Å)	28
Density(g/cm <sup>3</sup> )	2
pH(50g/l .H <sub>2</sub> O solution)	6
Specific area(m <sup>2</sup> /g)	737

The activated carbon was crashed and separated on molecular sieves .Four different granular sizes of activated carbon were obtained and classified according to their diameter ranges as follows:

A: (1000-2000), B: (500-1000), C: (250-500), D: (125-250) $\mu$ m

The granular activated carbon was dried at 105°C for 48 hours then placed in desiccator to be used in adsorption experiments.

Five different initial concentration solutions of Protocatechuic acid were prepared by adding 500ml deionized water to 0.5g pure phenolic compound (Protocatechuic acid) to obtain mother solution (1000ppm), then the five different concentrations were prepared from the mother solution by using the diluting with double deionized water. The five initial concentrations were:

(10,20, 30, 40, 50, ppm). Spectrophotometric instrument (SHIMADZU –UV-1700) was used to determine the maximum ultraviolet wavelength absorbance of Protocatechuic acid using scanning procedures and the appropriate wavelength was ( $\lambda_{max}=235nm$ ).

The adsorption process was performed using batch technique. In the adsorption experiments, 100 ml of the aqueous phase of each solution was poured in 500ml glass-stoppered flask and the flask was then placed in a shaker at room temperature. An amount of the carbon (0.1 g) was added into each flask. At that moment, the shaking was applied and the time recording was started. The aqueous samples (5 mL) were taken through filtration with 0.45 $\mu$ m filter at preset time intervals 15,60 min. Protocatechuic acid concentration in the liquid phase was determined with UV absorbance. The equilibrium concentrations were measured after 24 hours of continuous shaking.

## Results and discussion

### Adsorption equilibrium

Adsorption isotherms indicate distribution of adsorbate between solution and adsorbent when adsorption process reaches equilibrium state. When adsorption process reached equilibrium ,the pollutant concentration in the solution was  $C_e$  and the pollutant concentration in the solid phase  $q_e$  was calculated according to :

$$qe = \frac{Co-Ce}{m} v \quad (1)$$

Where,  $Co$ : the initial concentration of the pollutant in the solution(mmol/l).

$C_e$ : equilibrium concentration of the pollutant in the solution(mmol/l).

$m$ : the amount of solid phase(g). $v$ :the solution volume(l)

Then the relation between  $C_e$  versus  $q_e$  for every initial concentration and every granular size ,was plotted in fig(1).

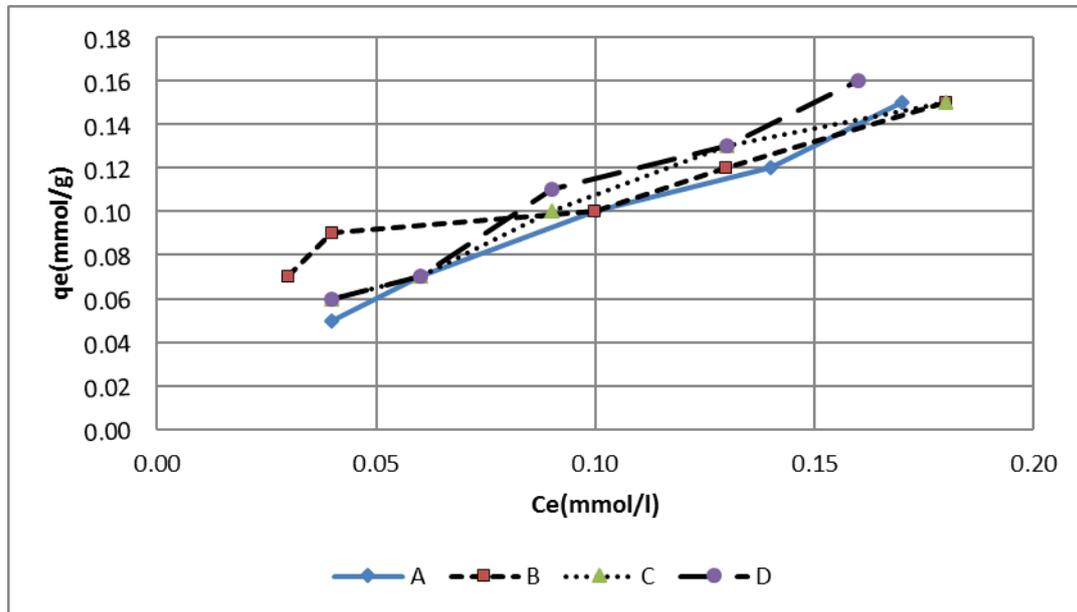


Figure (1): Adsorption isotherms of protocatechuic acid by activated carbon (contact time :24h, adsorbent dose: 0.1g/100ml)

Langmuir equation may be written as:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{1}{Q^0} C_e \quad (2)$$

where  $q_e$  is the amount of solute adsorbed per unit weight of adsorbent (mmol/ g),  $C_e$  the equilibrium concentration (mmol /L),  $Q^0$  the monolayer adsorption capacity (mmol /g) and  $b$  is the constant related to the free energy of adsorption ( $b \propto e^{-G/RT}$ ). It is the value reciprocal of the concentration of which half the saturation of the adsorbent is attained. The model parameters ( $Q^0$  and  $b$ ) can be determined from the linear plots of  $C_e/q_e$  and  $C_e$ .

The Freundlich model assumes heterogeneous surface energies, in which adsorption energy varies as a function of the surface coverage due to variation in the heat of adsorption. The Freundlich equation may be written as:

$$\text{Log} q_e = \text{Log} K_f + \frac{1}{n} \text{Log} C_e \quad (3)$$

where  $q_e$  is the amount of solute adsorbed per unit weight of adsorbent (mmol/ g),  $C_e$  the equilibrium concentration (mmol /L),  $K_f$  the constant indicative of the relative adsorption capacity of the adsorbent (mmol /g) and  $1/n$  is the constant, indicative of the intensity of the adsorption. The model parameters ( $K_f$  and  $1/n$ ) can be determined from the linear plots of  $\log q_e$  and  $\log C_e$ . The Freundlich model is widely applied in heterogeneous systems especially of organic compounds and highly interactive species on activated carbon and molecular sieves.

Table (2): Parameters for Langmuir and Freundlich equations

Adsorbent	Langmuir equation			Freundlich equation		
	$R^2$	$b(L/mmoll)$	$Q^0 (mmoll/g)$	$R^2$	$1/n$	$K_f(mmoll/g)$
A	0.96	4.03	0.36	0.96	0.73	0.75

B	0.96	11.59	0.23	0.98	0.46	0.61
C	0.97	4.56	0.34	0.99	0.71	0.76
D	0.97	4.73	0.35	1.00	0.72	0.79

As shown from table (2), The values of  $1/n$  ranged between 0-1 indicated that activated carbon can adsorb protocatechuic acid effectively. The value of  $Q^0$  was the highest for the granular size A (0.36 mmol/g), which refers to the best mixing conditions in case of granular size A.

### Adsorption kinetics

Figure (2) (a, b, c, d, e) shows typical time profiles for adsorption of Protocatechuic acid on different carbon particle sizes and at different initial adsorbate concentrations ( $C_0$ ) (10, 20, 30, 40, 50 ppm). It was found that the quantity of adsorbate, which was removed from the solution, increased as the initial concentration of the pollutant in the solution increased. The granular size of the adsorbent B had its higher removal average at initial concentrations (10, 20, 30 ppm), while granular size C had its higher removal efficiency at initial concentration of Protocatechuic acid (40, 50 ppm). This can imply the efficiency of activated carbon at smaller granular sizes.

### Kinetic models

The adsorption rate of Protocatechuic acid was studied using different models.

Pseudo-first-order expressed as follows:

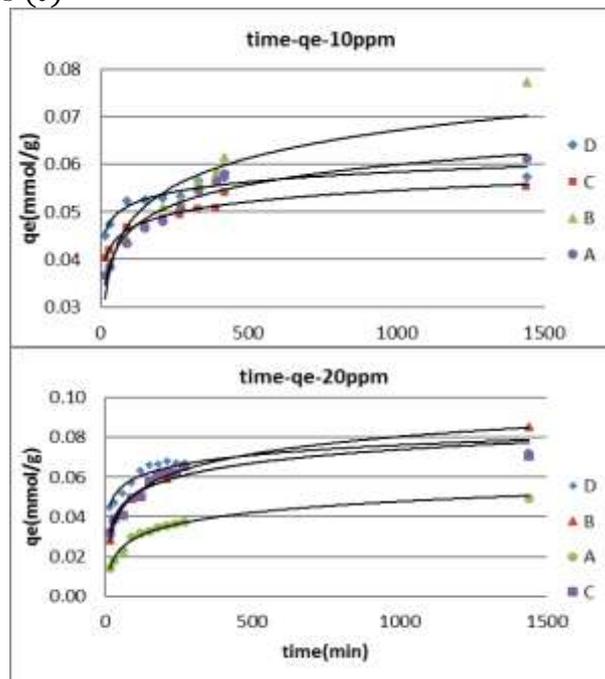
$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

Where:

$q_t$ : the adsorbed amount at time  $t$ .

$k_1$ : the first order rate constant.

$q_e$ : the adsorbed amount of adsorbate at the equilibrium, which is calculated by plotting the  $\log(q_e - q_t)$  versus ( $t$ )



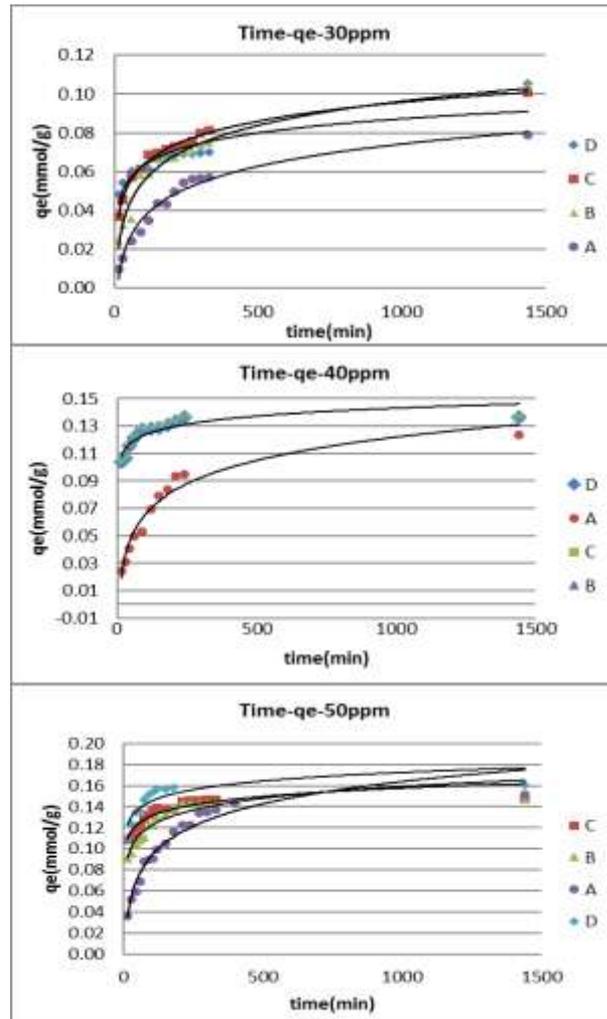
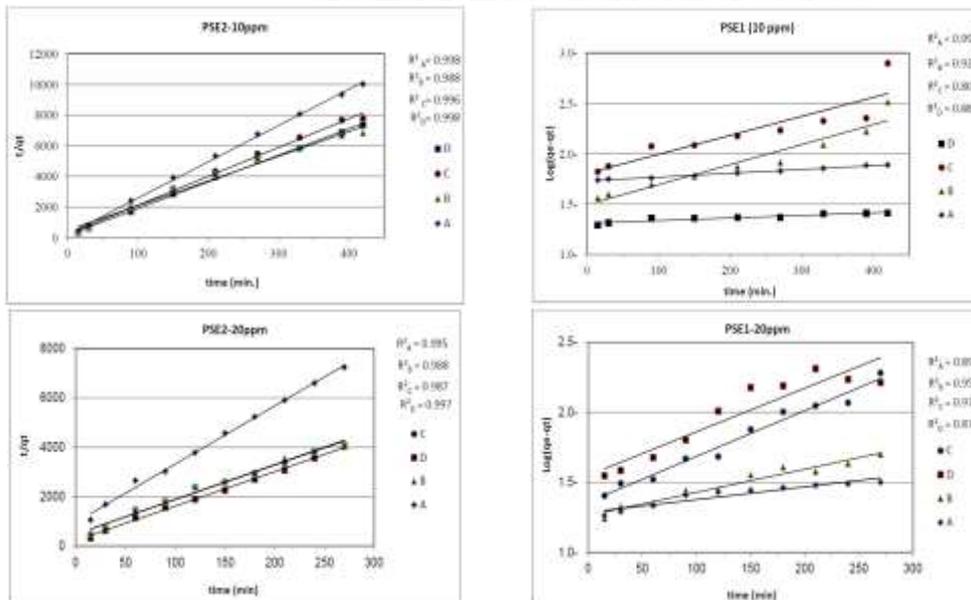
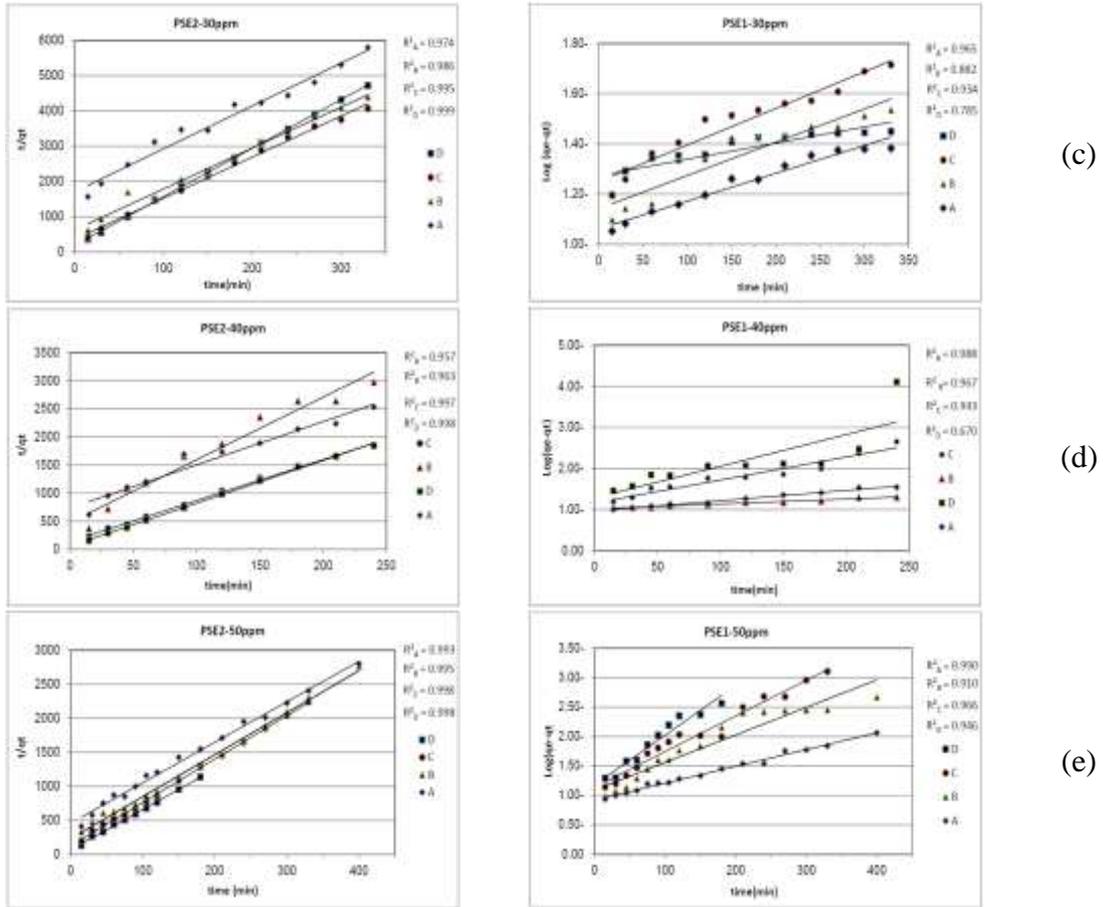


Figure (2): Time profiles for the adsorption of Protocatechuic acid at different carbon particle sizes and different initial concentrations of adsorbate.





**Figure (3):** The plots of Pseudo-first order equation and pseudo-second order equation of adsorption for the adsorption of Protocatechuic acid on four different particle sizes of activated carbon (A, B, C, D) at five initial concentrations of the adsorbate: a (10ppm), b (20ppm), c (30ppm), d (40ppm), e (50ppm).

The pseudo-second-order-equation based on equilibrium adsorption may be expressed as

$$\frac{t}{q_t} = \frac{1}{\vartheta_0} + \frac{1}{q_e} t \quad (5)$$

Where:

$q_t$ : the adsorbed amount at time  $t$ .

$q_e$ : the adsorbed amount at equilibrium.

$\vartheta_0$ : the initial sorption rate

The values of  $\vartheta_0, q_e$  can be calculated by plotting  $t/q_t$  versus  $t$ .

Figures (3) shows the plots which represent Pseudo-first-order and pseudo-second-order for the adsorption of protocatechuic acid at five different initial concentrations on four different sizes of activated carbon.

The table (3) shows that the values of  $q_e$ , which were calculated by the pseudo-second order equation, are very close to those measured experimentally. This is another evidence that the kinetic of the adsorption follows pseudo-second order. The adsorption rate  $\vartheta_0$  increased as the granular size of the adsorbent decreased; this can be interpreted by the film diffusivity of the adsorbate on the external surface of the particles of the adsorbent (Hameed and Rahman, 2008)

**Table 3: Pseudo- second order parameters at different initial concentrations of adsorbate and on different granular sizes of activated carbon.**

Co (ppm)	A		B		C		D	
	$\mathfrak{D}_0$	$q_e$	$\mathfrak{D}_0$	$q_e$	$\mathfrak{D}_0$	$q_e$	$\mathfrak{D}_0$	$q_e$
10	0.005	0.042	0.002	0.062	0.004	0.053	0.005	0.058
20	0.001	0.042	0.002	0.071	0.002	0.072	0.005	0.072
30	0.001	0.082	0.002	0.086	0.003	0.086	0.005	0.073
40	0.001	0.130	0.002	0.09	0.007	0.137	0.017	0.131
50	0.002	0.168	0.004	0.162	0.008	0.157	0.014	0.169

### Elovich rate equation

The equation defining the Elovich model is based on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption; which implies a multilayer adsorption. It is expressed by the relation ( Elovich and Larinov, 1962):

$$qt = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t) \quad (6)$$

Where  $qt$  is the concentration of adsorbate in the solid phase (mg/kg),  $a$  and  $b$  are the Elovich equation constants , and  $t$  is the time (min).

The empirical Elovich equation is most useful for determining adsorption rates and not sorption capacities, and it may be used to determine the effects of a pre-adsorbed gas (i.e., VOC) on the sequential adsorption of another gas (i.e., O<sub>3</sub>) (Low, 1960)

Either parameter  $a$  or  $b$  may be affected by pre-adsorption, assuming non-selective adsorption, that is, adsorption of the pre-adsorbate without the creation of a stratified adsorption zone (Low, 1960). Four basic types of pre-adsorption phenomena exist: enhancement ( $a$  increase and  $b$  decreases); poisoning ( $a$  decreases and  $b$  increases);pseudo-enhancement (both  $a$  and  $b$  decrease);and pseudo-poisoning (both  $a$  and  $b$  increase) (Low, 1960; Metts, 2006)

The Elovich rate equation is commonly used to describe the sorption behaviour with a rapid equilibrium rate in the early period, while it slows down the equilibrium at later periods of the sorption process. The constants  $a$  and  $b$  in the Elovich rate equations represent the rate of sorption and surface coverage, respectively (Teng, 1999), Alongside increasing initial concentrations, table (4) shows that the value of  $b$  decreases as initial concentration of the adsorbate increases due to the less available surface for protocatechuic acid. Furthermore, the value of  $a$  should increase with initial concentrations because of the higher driving force. However, this result was not reached in all cases in this study although the values of  $R^2$  of prediction fitted by the Elovich rate equation are rather high. The physical meaning should overwhelm the determination coefficient. Therefore, the Elovich rate equation may not be adequate to describe the kinetics of protocatechuic acid adsorbed onto the bigger granular sizes of the adsorbent (A, B) (Chang et al., 2004).

**Table (4): Elovich equation constants for the adsorption of protocatechuic acid with different initial concentrations on four different sizes of granular activated carbon.**

Co (ppm)	A			B			C			D		
	$R^2$	$a$	$b$	$R^2$	$a$	$b$	$R^2$	$a$	$b$	$R^2$	$a$	$b$
10	0.92	0.01	10.48	0.92	0.01	9.43	0.95	0.10	18.05	0.95	0.15	18.69
20	0.98	0.09	7.62	0.96	0.12	5.22	0.95	0.14	5.42	0.95	0.93	7.05
30	0.96	0.02	3.85	0.95	0.06	3.68	0.99	0.19	4.60	0.98	7.26	9.20

40	0.95	0.05	2.37	0.93	0.09	3.82	0.96	0.77	3.21	0.96	63.26	5.42
50	0.98	0.08	1.85	0.96	1.51	3.30	0.95	18.09	4.44	0.97	4.12	3.10

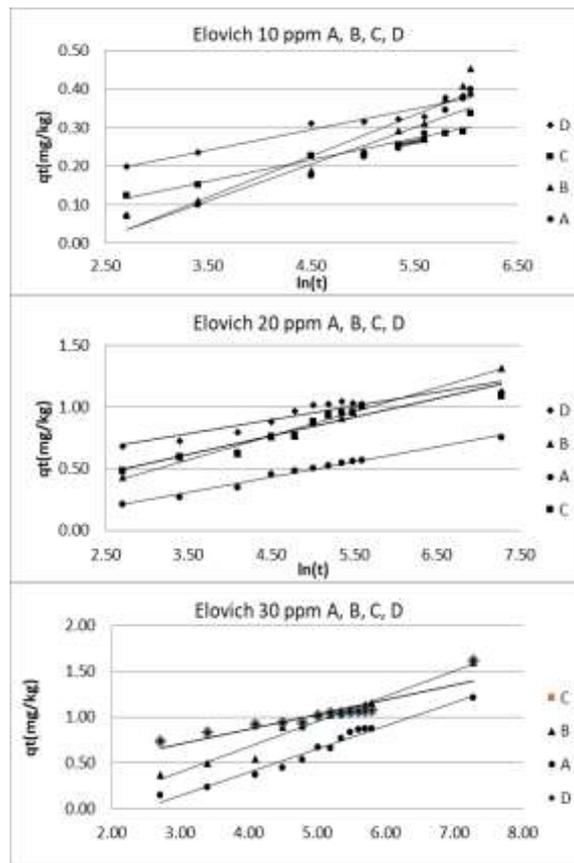
The validity of Elovich equation was checked by the linear plot of  $qt$  versus  $\ln t$ . The fitness is quantitatively determined from the normalized standard deviation  $\Delta q$ , defined as:

$$\Delta q\% = 100 \sqrt{\frac{\sum[(qt,exp-qt,cal)/qt,exp]^2}{(N-1)}} \quad (7)$$

where  $N$  is the number of data points (Wu et al, 2005).

The validity of Elovich equation was checked by using the  $\Delta q\%$  standard, which was calculated according to the equation (7). Table(5) shows that Elovich equation is valid for granular sizes of activated carbon C and D, in all initial concentrations of protocatechuic acid in the solution, according to the small values of  $\Delta q\%$  (less than 10%). In contrast, Elovich equation is found invalid for granular sizes of activated carbon A, B in all initial concentrations but only at some ones. In addition, table (6) shows that the  $q_e$  values, calculated by using Elovich equation, were very close to the experimental ones. The results suggest that the adsorption is rate-determined by chemisorptions step in the smaller granular sizes of activated carbon (Cheung et al., 2001; Juang and Chen, 1997).

The validity of the Elovich equation suggests that the chemisorption (chemical reaction) mechanism plays a certain role in the present processes (Juang et.al, 2006)



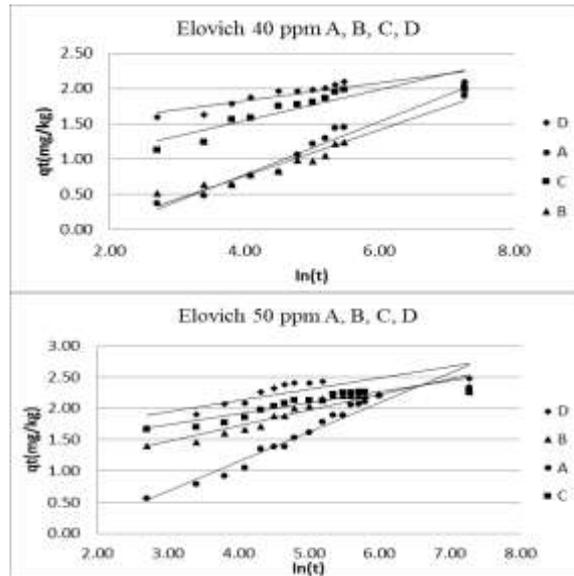


Figure 4: Plots of the Elovich kinetic model at different initial protocatechuic Acid concentrations adsorbent dose, 100 mg/100 ml, for four different granular sizes of activated carbon (A,B,C,D).

Table (5): The values of  $\Delta q\%$  for the four different sizes of granular adsorbent(activated carbon) with five different initial concentrations of adsorbate (protocatechuic acid).

Co (ppm)	$\Delta q\%$			
	A	B	C	D
10.0	21.0	21.8	5.6	4.4
20.0	5.2	5.1	6.2	3.8
30.0	19.6	10.4	2.0	1.7
40.0	15.9	8.7	9.1	2.0
50.0	7.9	3.4	2.4	9.1

Table (6): The amount of Protocatechuic acid ( $q_e$ ), adsorbed on four different sizes of activated carbon (A, B, C, D) at five different initial concentrations  $C_o$ , measured experimentally and calculated by using pseudo-first order and pseudo-second order and elovich equations.

(ppm) $C_o$	A				B				C				D			
	(exp)	(pse-1)	(pse-2)	elovich												
10	0.05	0.177	0.042	0.063	0.06	0.224	0.062	0.016	0.06	0.165	0.053	0.056	0.06	0.27	0.058	0.061
20	0.07	0.276	0.042	0.052	0.09	0.282	0.071	0.096	0.07	0.257	0.072	0.084	0.07	0.212	0.072	0.084
30	0.1	0.346	0.082	0.081	0.1	0.32	0.086	0.101	0.1	0.287	0.086	0.101	0.11	0.28	0.073	0.082
40	0.12	0.381	0.13	0.14	0.13	0.362	0.09	0.106	0.13	0.314	0.137	0.166	0.13	0.277	0.131	0.157
50	0.15	0.397	0.168	0.188	0.15	0.335	0.162	0.175	0.15	0.32	0.157	0.171	0.16	0.307	0.169	0.206

The table (6) shows that the values of  $q_e$ , which were calculated by pseudo-second order equation are very close to those, which were measured experimentally. That is another approval that the kinetic of the adsorption follows pseudo-second order.

#### Intra particle diffusion model

Intra-particle equation :

$$qt = kpt^{0.5} + c \quad (8)$$

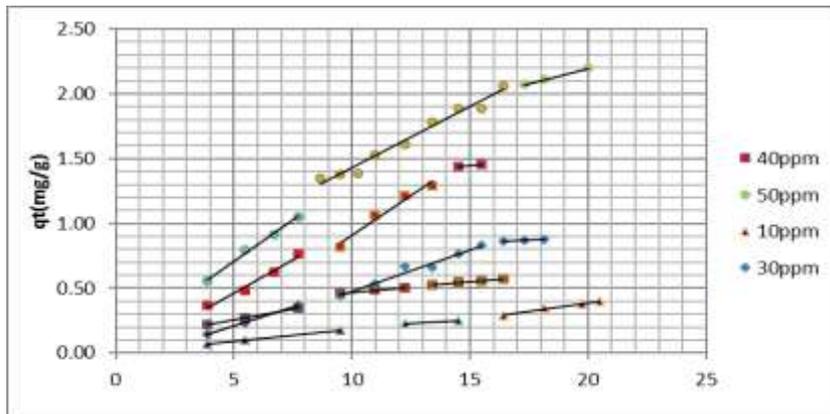
where  $kp$  is the intra-particle rate constant ( $mg/g.min^{-0.5}$ ) (Wei Ma et al., 2007)

the intra-particle rate constant  $k_p$  is a function of equilibrium concentration in solid phase  $q_e$  and intra-particle diffusivity  $D$  in the following way:

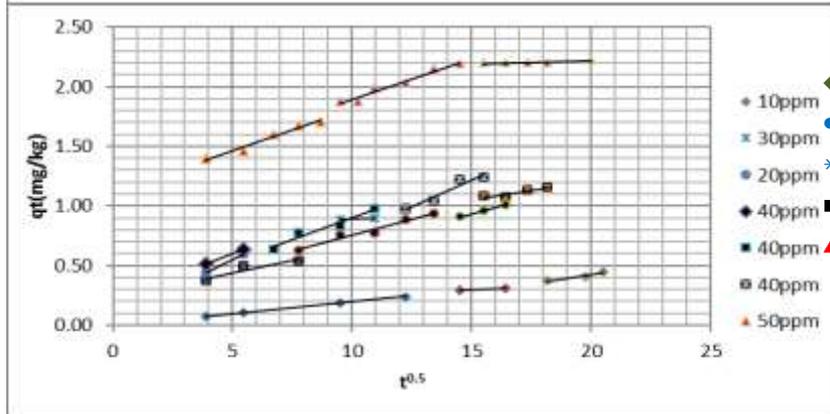
$$Kp = (6qe/R)(D/\pi)^{0.5} \quad (9)$$

where  $R$  is the particle radius (Wang et al., 2007).

As shown in figure (5; a, b, c, d) . By the plots of  $q_t$  versus  $t^{0.5}$  of various protocatechuic acid concentrations, multilinearities were observed in indicating that three steps took place. The first portion was the sharpest one which can be attributed to the diffusion of protocatechuic acids through the solution to the external surface of adsorbent. The second portion described the gradual adsorption stage where intraparticle diffusion was rate limiting. The third portion was attributed to the final equilibrium stage in which the intraparticle diffusion started to slow down due to the extremely low adsorbent concentration left in the solution. The rate of uptake might be limited by the size of adsorbate molecule, concentration of the adsorbate and its affinity to the adsorbent, diffusion coefficient of the protocatechuic acid in the bulk phase, and the pore-size distribution of the adsorbent. The slope of the linear portion indicated the rate of the adsorption. The lower slope corresponded to a slower adsorption process. It can be observed that the diffusion in the bulk phase to the exterior surface of adsorbent, which



A



B

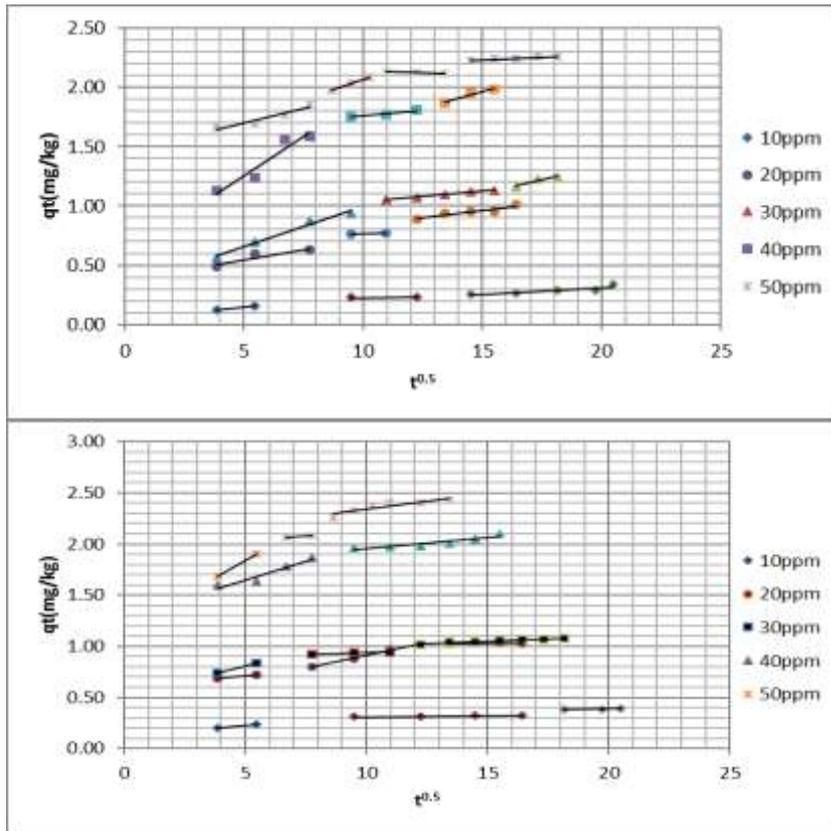
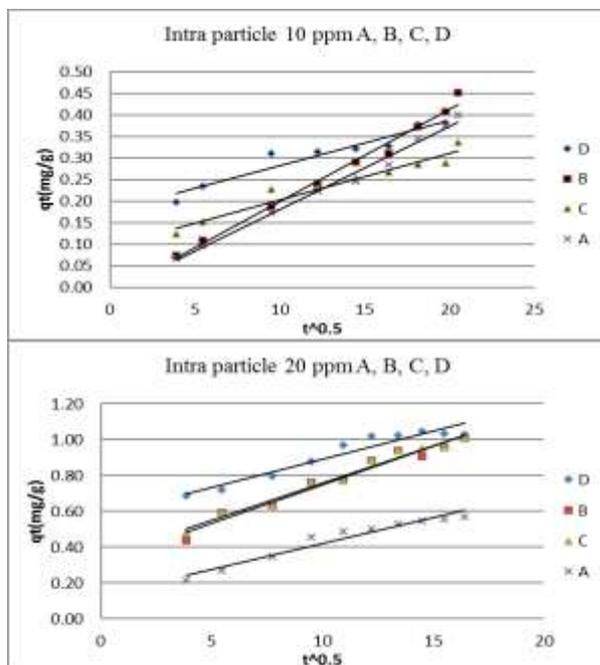


Figure (5): The plot of intra particle diffusion model of four granular sizes(A,B,C,D) of activated carbon using five different initial concentration of portocatechuic acid.



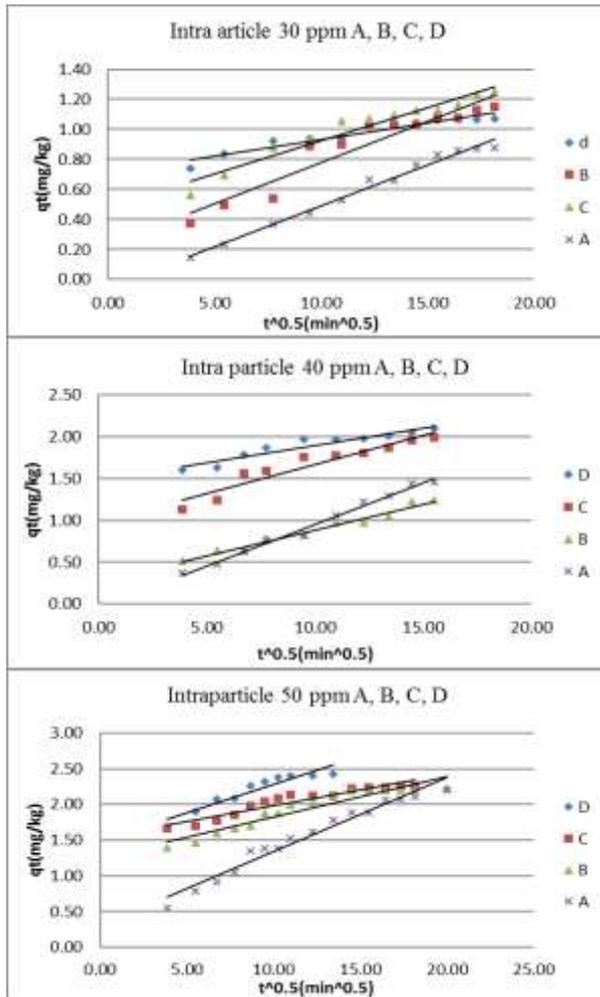


Figure (6): plots represent intra particle diffusion model ( qt versus  $t^{0.5}$ )for adsorption of portocatechuic acid at five different initial concentration onto four granular sizes of activated carbon.

started at the onset of the process, was the fastest. The second portion of the plot could refer to the diffusion into mesopores and the third one, with the lowest slope, may refer to adsorption into micropores. This implied that the intraparticle diffusion of adsorbent molecules into micropores was the rate-limiting step in the adsorption process on activated carbon (Cheung et.al, 2007).

As the lines don't cross the zero point, which can be explained by ,intra particle diffusion is not the only step during the whole adsorption process, but only one was rate limiting in any particular time range (Mohana et.al., 2002).

Table (7): Intra particle equation parameters for the adsorption of protocatchuic acid at five initial concentration on four granular sizes of activated carbon.

Intial conc. Co(ppm)	A			B			C			D		
	R <sup>2</sup>	k <sub>p</sub>	D (μm <sup>2</sup> /min)	R <sup>2</sup>	k <sub>p</sub>	D (μm <sup>2</sup> /min)	R <sup>2</sup>	k <sub>p</sub>	D (μm <sup>2</sup> /min)	R <sup>2</sup>	k <sub>p</sub>	D (μm <sup>2</sup> /min)
10	0.99	0.02	357.26	0.99	0.02	45.85	0.95	0.01	11.04	0.92	0.01	2.11
20	0.95	0.03	281.82	0.96	0.04	51.82	0.97	0.04	17.95	0.92	0.03	2.27
30	0.98	0.05	398.14	0.91	0.06	58.19	0.94	0.04	10.01	0.92	0.02	0.53
40	0.99	0.10	539.55	0.97	0.06	46.69	0.91	0.07	14.56	0.91	0.04	1.12
50	0.96	0.10	388.74	0.90	0.06	31.32	0.91	0.04	4.73	0.90	0.08	3.03

As table(7) shows, the values of diffusivity constants  $D$ , which were calculated by using equations 8, 9 where  $K_p$  was the slope of line ( $qt$  vs.  $t^{0.5}$ ) then  $D$  were calculated by using equation 9 with respect to the different radius of activated carbon granular sizes, are different according to the granular sizes of the adsorbent (A, B, C, D) as following:  $D(A) > D(B) > D(C) > D(D)$ ; this result indicates that the size of the granular adsorbent plays an important role in defining the rate controlling step in the adsorption process. Using equation (5), one interpretation is that the diffusivity values are proportional to the square of radius of the granular adsorbent. The higher values of effective particle diffusivity for bigger granular sizes of adsorbent indicates that the solute can reach the active sites, within the internal matrix of adsorbent particles, quicker than in smaller ones (Wu et al., 2005).

As initial protocatechuic acid concentration increased the intra particle rate constant  $k_p$  increased. It could be interpreted as follows: the intra-particle rate constant  $k_p$  is a function of equilibrium concentration in solid phase  $q_e$  (Wang et al., 2007).

## Conclusion

The adsorption of protocatechuic acid on activated carbon was investigated in batch experiment. Kinetic study of adsorption was hold. This work confirms that activated carbon is suitable adsorbent for the removal of protocatechuic acid from olive mill waste water. The results of kinetic modeling show that the pseudo-second-order kinetic model was better described the time effect on the protocatechuic acid adsorption than the pseudo-first-order model.

As the constant  $a$  in Elovich equation didn't increase by initial concentration of adsorbate increasing, this equation didn't fit the adsorption in spite of it was valid the validity was achieved for two granular sizes of activated carbon C, D at all initial concentration of protocatechuic acid. Intra particle diffusion model describes the kinetic of the process by multilinearities of the plots which indicates that the process was in three steps. The values of diffusivity constant  $D$  increases as the size of adsorbent increases. As shown from results that the kinetic fit Pseudo second order and intra particle diffusion model, which suggest the chemo sorption mechanism and diffusion of pollutant through the film surrounding the particles of adsorbent. the results induce to continue the kinetic study using more models like film pore diffusion model or other to characterize the adsorption precisely.

## References

- ABDELKREEM, M. *Adsorption of Phenol from Industrial Wastewater Using Olive Mill Waste*. Apcebe Procedia 5 (2013), 349–357.
- AGRIOS, A.; GRAY, K.; WEITZ, E *Photocatalytic Transformation of 2,4,5-Trichlorophenol on TiO<sub>2</sub> under Sub-Band-Gap Illumination*. Langmuir 19, (. 2003), 1402–1409.
- BARBEAU, L.; DESCHENES, D.; KARAMANEV, Y.; COMEAU, R. S. *Bioremediation of Pentachlorophenol Contaminated Soil by Bio-Augmentation Using Activated Soil*, Appl. Microbiol. Biotechnol, 48, (1997), 745–752.
- BUCHANAN, I.D. AND MICELL, J. A. *Peroxidase Catalyzed Removal of Aqueous Phenol*, Biotechnol. Bioeng, Vol. 54, (1997), 251–261.
- BURLEIGH, M.C.; MARKOWITZ, M.A.; SPECTOR, M.S.; GABER, B. P. *Porous Polysilsesquioxanes for the Adsorption of Phenols*, Environ. Sci. Technol, Vol. 36, (2002), 2515–2518.

- CHANG, C.F.; CHANG, C.Y.; , CHEN, K.H.; TSAI, W.T.; SHIE, J.L.; CHEN, Y.H. *Adsorption of Naphthalene on Zeolite from Aqueous Solution*, Journal of Colloid and Interface Science, 277, (2004), 29–34.
- CHEUNG, C.W.; PORTER, J.F.; MCKAY, G. *Sorption Kinetic Analysis for the Removal of Cadmium Ions from Effluents Using Bone Char*, Water Research, 35, (3), (2001), 605–612.
- CHEUNG, W.H.; SZETO, Y.S.; MCKAY, G. *Intraparticle Diffusion Processes during Portric Acid Adsorption onto Chitosan*, Bioresource Technology, Vol. 98, (2007), 2897–2904.
- DAVIS, S. and BURNS, R. G. *Covalent Immobilization of Laccase on Activated Carbon for Phenolic Treatment*. Appl. Microbiol. Biotechnol, Vol. 37, (1992), 474–479.
- DEMARCO, E.; SAVARESE, M.; PADUANO, A.; SACCHI, R. *Characterization and Fractionation of Phenolic Compounds Extracted from Olive Oil Mill Wastewaters*, Food Chemistry, Vol. 104, (2007), 858–867.
- El-Naas, M.H.; Al-Zuhair, S.; Abu Alhaija, M. *Removal of Phenol from Petroleum Refinery Wastewater through Adsorption on Date-Pit Activated Carbon*, Chemical Engineering Journal, Vol. 162, (2010), 997–1005.
- ELOVICH, S.Y. and LARINOV, O.G. *Theory of Adsorption from Solutions of Non Electrolytes on Solid (I) Equation Adsorption from Solutions and the Analysis of Its Simplest Form, (II) Verification of the Equation of Adsorption Isotherm from Solutions*, Izvestiya Akademii Nauk. SSSR, Otdelenie Khimicheskikh Nauk, Vol. 2, (1962), 209–216.
- HAMEED, H. AND RAHMAN, A. A. *Removal of Phenol from Aqueous Solutions by Adsorption onto Activated Carbon Prepared from Biomass Material*, J. Hazard. Mater, 160, (2008), 576–581.
- HEA, J.; BRIGGSC, M.A.; LYSTERC, T.; JONESB, G. P. *Stability and Antioxidant Potential of Purified Olive Mill Wastewater Extracts*, Food Chemistry, Vol. 131, (2012), 1312–1321.
- HENINIA, G.; LAIDANIA, Y.; SOUAHIB, F.; HANINIC. *Study of Static Adsorption System Phenol / Luffa Cylindrica Fiber for Industrial Treatment of Wastewater*, Energy Procedia, Vol. 18, (2012), 395–403.
- JUANG, R.S. AND CHEN, M. L. *Application of the Elovich Equation to the Kinetics of Metal Sorption with Solvent-Impregnated Resins*, Industrial and Engineering Chemistry Research, Vol. 36, (1997), 813–820.
- JUANG, R.S.; LIN, S.H.; CHENG, C.H. *Liquid-Phase Dsorption and Desorption of Phenol onto Activated Carbons with Ultrasound*, Ultrasonics Sonochemistry, Vol. 13, (2006), 251–260.
- KULKARNI, S.J., TAPRE, R.W., PATIL, S.V.; SAWARKAR, M, B. *Adsorption of Phenol from Wastewater in Fluidized Bed Using Coconut Shell Activated Carbon*, Procedia Engineering, Vol. 51, (2013), 300–307.
- KUNWAR P.S.; MALIK, A.; SINHA, S.; OJHA, P. *Liquid-Phase Adsorption of Phenols Using Activated Carbons Derived from Agricultural Waste Material*, Journal of Hazardous Materials, Vol. 150, No, 3, (2008), 626–41.
- LEYVA, E.; MOCTEZUMA, E.; RUIZ, M.G.; TORRESMARTINEZ, L. *Photo-Degradation of Phenol and 4-Chlorophenol by BaO–Li<sub>2</sub>O–TiO<sub>2</sub> Catalysts*, Catal. Today, Vol. 40, (1998), 367–376.
- LOW, M. *Kinetics of Chemisorption of Gases on Solids*, Chem. Rev., Vol. 60, No. 3, (1960), 267–312.

- MA, W.; YA, F.Q.; HAN, M.; WANG, R. *Characteristics of Equilibrium, Kinetics Studies for Adsorption of Fluoride on Magnetic-Chitosan Particle*, Journal of Hazardous Materials, Vol. 143, No, 1–2, (2007), 296–302.
- METTS, T.A. and BATTERMAN, S. A. *Effect of VOC Loading on the Ozone Removal Efficiency of Activated Carbon Filters*, Chemosphere, Vol. 62, (2006), 34–4.
- MOHANA, S.V.; RAOA, N.C.; KARTHIKEYAN, J. *Adsorptive Removal of Direct Azo Dye from Aqueous Phase onto Coal Based Sorbents: A Kinetic and Mechanistic study*, Journal of Hazardous Materials, Vol. 90, (2002), 189–204.
- MORENO, C. C. *Adsorption of Organic Molecules from Aqueous Solutions on Carbon Materials*, Carbon, Vol. 42, (2004), 83–94.
- PANDIT, A.B.; GOGATE, P.R.; MUJUMDAR, S. 2001. *Ultrasonic Degradation of 2:4:6 Trichlorophenol in Presence of TiO<sub>2</sub> Catalyst*. Ultrason Sonochem 8, (2001), 227–231.
- RADOVIC, L.R.; MORENO, C. C.; RIVERA U. J. *Carbon Materials as Adsorbents in Aqueous Solutions*, Chemistry and Physics of Carbon, Vol. 27, (2001), 227–405.
- SHIRGAONKAR, I.Z. AND PANDIT, A. B. *Sonophotochemical Destruction of Aqueous Solution of 2,4,6-Trichlorophenol*, Ultrason. Sonochem, Vol. 5, (1998), 53–61.
- TENG, H.; HSIEH, C.T. *Activation Energy for Oxygen Chemisorption Oil Carbon at Low Temperatures* Ind. Eng. Chem. Res., Vol. 38, (1999), 292–297.
- THOMAS, S.Y.; CHOONG, T.N.; WONG, T.G.; IDRIS, C.A. *Film-Pore-Concentration-Dependent Surface Diffusion Model for the Adsorption of Dye onto Palm Kernel Shell Activated Carbon*, Journal of Colloid and Interface Science, Vol. 301, (2006), 436–440.
- WANG, Y.; GAO, B. Y.; YUE, W.W.; YUE, Q.Y. *Adsorption Kinetics of Nitrate from Aqueous Solutions onto Modified Wheat Residue*, Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 308, No, 1–3, (2007), 1–5.
- Wu, F.C.; Tseng, R.L.; Juang, R.S. *Preparation of Highly Microporous Carbons from Fir Wood by KOH Activation for Adsorption of Dyes and Phenols from Water*, Separation and Purification Technology, Vol. 47 (2005), 10–19.