Removal of Pesticide (Oxamyl) from Water using Activated Carbons Developed from Apricot Stones

Th. El-Nabarawy¹, S. A. Sayed¹ Ahmed and A. M. Youssef^{2,▲}

¹National Research Centre, Dokki, Cairo, Egypt

²Faculty of science, Mansoura University, Egypt

▲e-mail: amayosef@mans.edu.eg

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Abstract

Four stream- activated carbons were prepared by carbonizing apricot stones at 600°C followed by gasification with steam at 950°C to burn-off's = 17, 32, 49 and 65%. The textural parameters of these activated carbons were determined from nitrogen adsorption results at 77 K. The total pore volume and the mean pore radius increased with the increase of % burn-off whereas the surface area increased with the increase of burn-off from 17 to 32 and further to 49%. Further increase of burn-off to 65% was associated with a considerable decrease in surface area as a result of pronounced pore widening due to pore erosion. The surface pH values of the carbons investigated range between 7.1 and 8.2. The adsorption of oxamyl onto the activated carbon followed pseudo-second order kinetics and the equilibrium adsorption isotherms fitted Langmuir adsorption model. The adsorption of oxamyl proved to be of the physical type and took place in non-micropores. The amount of oxamyl adsorbed expressed as q_m depends to a large extent to the surface area located in non-micropores S^∞_m , where a straight line relationship passing through the origin was obtained.

Keywords : Pesticide, Activated Carbons, Apricot Stones

1. Introduction

Environmental pollution has become a major issue in agriculture during the past several years because the increased use of pesticides has led to a greater emphasis on serious environmental contamination. The frequent detection of pesticides in surface and ground water [1, 6] has increased interest in finding the proper technique for the removal of pesticides from water either completely or by minimizing their concentrations down to the safe level.

The technique of adsorption has been found to be a useful means for controlling the extent of water pollution due to dyes, metallic species, organic pollutants and pesticides [7, 12]. The major advantages of adsorption system for water pollution control are less investment in terms of initial cost and land [13, 14], simple design [15] and easy operation [16, 17]. It also has the advantage of superior removal of organic waste contaminants compared to the biological treatment processes [18]. Among adsorbents used for water pollution control, adsorption by activated carbons (ACs) proved to be the most efficient. ACs relate to a group of materials with highly developed surface area and porosity and have a large adsorption capacity for various adsorptive both from solutions and from gaseous phase [19, 20]. ACs also find a use in catalysis where they may be used as catalysts [21] or as catalyst supports [22]. The treatment of surface and

wastewater are new important fields in which ACs are very effective [23].

ACs can be produced from any carbonaceous material precursor, both naturally occurring and synthetic. Common examples of commercial feedstocks are materials of botanical origin (e.g. wood, coconut shell, nut kernels, rice straw, fruit stones, corn cobs, cotton stalks and others) and degraded or coalified materials. ACs are obtained by following one of two procedures: chemical activation or physical activation. In chemical activation, the precursor in a divided form is mixed with an activating agent such as zinc chloride, phosphoric acid or potassium salts and the mixture is then carbonized in absence of air or in an inert atmosphere not exceeding 1000 K [24]. Physical activation is more frequently used and is performed by gasifying non-activated carbon with a stream of oxidizing gas to a certain degree of burn-off [25].

Ethanimidothioic acid 2- (dimethylamino)-N-(((methylamino) carbonyl) oxy)-2-oxo-methyl ester [(CH₃)₂N-C-C(=N)-O-C-NHCH₃] is a broad leaf, non-volatile, insecticide, menatocide which has been widely used in agriculture for a long time for the control of nematode problems which have been developed in crops production. The frequent detection of pesticides including oxamyl in ground and surface water has increased experimental studies on pesticide adsorption by soils. However, the data on pesticide adsorption by ACs

are still limited and further investigations are still required in this concern.

The major purposes of the present work was to: (i)- determine the kinetics of adsorption of oxamyl from aqueous solution using steam- activated carbons with various percentages of burn-off. (ii)- determine the adsorption capacities of ACs for this pollutant and the change of the adsorption capacity in the temperature range 298-318 K, i.e at temperatures around the ambient temperature in many countries and meanwhile to determine the thermodynamic parameters of oxamyl adsorption by ACs. (iii) relate the oxamyl adsorption capacity to some of the textural parameters of ACs investigated.

2. Experimental

2.1. Materials

Dry clean apricot stones were crushed to a particle size of 0.6-1.5 mm in diameter before carbonization in absence of air at 600°C. The rate of heating was 10 K/min and the sample was soaked at 600°C for 2 h. The textural parameters of "C" were determined in a previous work to be the surface area=288 m²/g; the total pore volume 0.132 mL/g and the mean pore radius=0.92 nm. The carbonization product "C" was used for the preparation of steam-activated carbons "CS". Portions of "C" were gasified with a mixture of nitrogen and steam at 950°C in a tubular muffle furnace to burn-off's=17, 32, 49 and 65% to give ACs designated CS17, CS32, CS49 and CS65, respectively. Details of steam-activation are given elsewhere [25].

Oxamyl, a product of Du Pont (Wilmington, Dela.) was used as received. Other reagents including CuSO₄, 5H₂O, CH₃COONH₄, NH₄OH, NaOH, CS₂, KOH and CH₃COOH, were BDH analytical grade.

2.2. Techniques

The textural properties of the activated carbons were determined from nitrogen adsorption at 77 K using conventional volumetric apparatus. Prior to any adsorption measurement, the AC sample was degassed at 200°C for 6 h under a reduced pressure of 10⁻⁵ Torr. The surface pH of the carbons and also of the aqueous solution of oxamyl were measured using digital pH meter (pope model No 1501). The kinetic adsorption of oxamyl by ACs at 298 K were undertaken by determining the amounts of oxamyl adsorbed per one gram adsorbent at different intervals of time up to 6 h. The equilibrium adsorption was undertaken using the batch shaking technique. Suitable aliquots (1-10 mL) of an aqueous solution of oxamyl were introduced into different 50 mL glass conical flasks which were then stoppered. Each experiment was conducted in duplicate and each isotherm

Fig. 1. Adsorption isotherms of N₂ at 77 K onto ACs investigated.

determination involved 21 flasks for each of 10 oxamyl doses plus one as a blank containing the carbon sample with no oxamyl. The suspensions were shaken in an incubator at 298, 305, 313 and 318 K. Each suspension was centrifuged for 10 min at 5000 rpm, the supernatant liquid was collected and estimated spectrophotometrically. Details of oxamyl determination are reported elsewhere [26].

3. Results and discussion

3.1. Textural properties

The adsorption of nitrogen on ACs investigated at 77 K proved to be rapid with the equilibrium attained within 30 min. The nitrogen adsorption isotherms are shown in Fig.1. The shape of the isotherm changed with the change of the degree of gasification of the carbon with steam, i.e. with the percentage burn-off. Thus, the nitrogen adsorption isotherm of CS17 was typical type I according to the BDDT classification [27]. CS65 exhibited, on the other hand, typical type II in the same classification. CS32 and CS49 exhibited nitrogen adsorption isotherms showing both the characteristics of type I and type II. The nitrogen adsorption isotherms were analyzed using the BET equation [28], which allowed the determination of the surface area S_{BET} (m²/g), adopting the value of 0.162 nm² for the cross-sectional area of nitrogen at 77 K. The total pore volume of each carbon, V_T (mL/g) was read from the amount of nitrogen adsorbed very close to saturation i.e. at $P/P_o \approx 0.98$ as shown on the isotherm. Another important textural parameter, namely the mean pore radius r_m (nm) could be obtained from the relationship.

$$\bar{r}(\text{nm}) = \frac{2V_T(\text{mL/g})}{S_{BET}(\text{m}^2/\text{g})} \quad (1)$$

The values of S_{BET} , V_T and r_m are listed respectively in columns 2, 3 and 4 of Table 1. Another independent method, namely, the α -method [29] was also used to analyze the nitrogen adsorption isotherms. The α -plots of nitrogen adsorption are depicted in Fig. 2. The α -method allowed also

Table 1. Textural properties of the activated carbons

Carbon	S_{BET} m ² /g	V_T mL/g	r_m nm	s m ² /g	S_n^a m ² /g	S_m^a m ² /g	V_n^a mL/g	V_m^a mL/g
CS 17	725	0.448	1.24	750	210	540	0.138	0.310
CS 32	949	0.769	1.63	940	584	356	0.610	0.159
CS 49	970	1.178	2.43	950	672	278	1.038	0.140
CS 65	754	1.318	3.49	736	656	80	1.287	0.031

the determination of the surface area α_s (m²/g), the surface areas located in micropores (S_m^a) and those located in non-micropores (S_n^a). Another advantage of the α -method is the possibility of estimation of the micropore volume of the adsorbent V_m^a and the non-micropore volume V_n^a . The standard data of nitrogen adsorption at 77 K by a non-porous carbon [30] were used in the analysis of the present nitrogen adsorption isotherms. α_s , S_n^a , S_m^a , V_n^a and V_m^a are listed in column 5, 6, 7, 8 and 9 of Table 1, respectively.

Inspection of Table 1 reveals that: (i) the surface areas of ACs as determined by the application of the α -method (α_s) are comparable to those determined from the BET method S_{BET} . (ii) The total pore volume and the mean pore radius increased with the increase of % burn-off. The surface area, on the other hand, considerably increased with the increase of % burn-off from 17 to 32%. However, further increase of the % burn-off from 32 to 49% was associated with a slight increase in the surface area, i.e. with about 4% only. Moreover, further rise of burn-off to 65% resulted in a noticeable decrease in the surface area, i.e. with approximately 29%. (iii) The changes in the textural properties with the change in the percentage of burn-off probably indicated that at low burn-off, the activation with steam is associated with creation of new micropore, and slight widening to the existing ones. Steam-activation to higher percentages of burn-off, i.e. between 30 and 50% is associated with pore widening more than creation of micropores. Further increase of burn-off is probably associated with intensive erosion of the pores which may lead to a decrease in the surface area.

3.2. Effect of pH

Among the factors determining the adsorption of an adsorptive from its aqueous solution, the pH and equilibrium time are the most important. Preliminary experiments have been carried out to determine the proper pH which leads to maximum oxamyl sorption. Evidently, when all other adsorption condition are same except solution pH, maximum oxamyl sorption took place from solutions of pH=6.8. This was true for all the carbons investigated in this work. Adsorption kinetics and adsorption isotherms of oxamyl were undertaken at pH=6.8.

3.3. Adsorption kinetics

The rate of oxamyl adsorption by the activated carbons at

298 K is presented in Fig. 3. It is apparent from the kinetic curves obtained that the equilibrium time was more or less the same which may be ascribed for the similarity of the sorbents, all are prepared from the same precursor and were activated by following the same technique. The attainment of equilibrium was relatively fast being within approximately the first hour of adsorption. The data depicted also show that the rate of oxamyl adsorption was very rapid initially, decreasing markedly between 10 and 60 min, and

Fig. 2. Plots of N₂ adsorption at 77 K onto ACs investigated.

Table 2. Kinetic parameters of the adsorption of oxamyl at 298 K onto the activated carbons

Carbon	K_1 (min^{-1})	q_{max} mg/g	R^2_1	$K_2 \times 10^3$ g/(mg min)	q_{max} mg/g	R^2_2	K_p mg ($\text{g min}^{0.5}$) ²	R^2_p
CS 17	32.6	4.17	0.9989	5.9	4.67	0.9907	0.39	0.9995
CS 32	36.2	13.90	0.9993	2.3	13.33	0.9899	1.05	0.9990
CS 49	26.4	14.97	0.9197	2.5	14.17	0.9903	1.18	0.9992
CS 65	29.9	14.70	0.9197	2.6	13.50	0.9903	1.25	0.9971

thereafter gradually approaching equilibrium.

Three kinetic models, i.e. the pseudo- first-order equation [31] [equation (1)], the pseudo-second-order equation [32] [equation (2)] and as intraparticle diffusion equation [33] [equation (3)], were considered to interpret the experimental data.

$$\frac{1}{q_t} = \left[\frac{K_1}{q_{\text{max}}} \right] \left[\frac{1}{t} \right] + \frac{1}{q_{\text{max}}} \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_{\text{max}}^2} + \frac{1}{q_{\text{max}}} t \quad (2)$$

$$q_t = k_p t^{0.5} \quad (3)$$

where q_t is the amount of oxamyl adsorbed (mg/g) at various times t (min), q_{max} is the maximum adsorption capacity (mg/g), K_1 (min^{-1}) is the rate constant of the pseudo-first-order model for the adsorption process, K_2 [g/ (mg min)] is the rate constant of the pseudo-second-order model for the adsorption process and K_p is the intraparticle diffusion rate constant. All three models, adequately described the adsorption kinetics. Figure 4 demonstrates the application of

the pseudo-first-order model to the adsorption data of oxamyl at 298 K. The linear plots obtained allowed the determination of K_1 for each oxamyl- carbon system and the correlation coefficient R^2 determining the validity of the pseudo-first-order model. The values thus obtained are listed in Table 2.

In the present studies linear plots were obtained for oxamyl adsorption results onto the ACs when pseudo-first-order model was applied (Fig. 4). However the experimental values of q_{max} were not equal to the calculated values. Also, the values of correlation coefficients of oxamyl adsorption onto CS49 and CS65 as obtained by the application of pseudo-first-order model are low, i.e., 0.9197 (Table 2). This may indicate that adsorption of oxamyl on the ACs investigated did not proceed via pseudo-first-order reaction. Very satisfactory linear plots were obtained upon application of pseudo-second-order-rate equation (Fig. 5). The experimental q_{max} values were in good agreement with the corresponding calculated values and the R^2 were all approaching unity (Table 2). This favors the assumption that the adsorption of oxamyl on the ACs investigated proceeded via pseudo-second-order kinetics.

Intraparticle diffusion may be the rate- controlling step. If this does occur, then the plots of q_t versus $t^{0.5}$ should be linear and if it passes through the origin then intraparticle diffusion will be the sole rate-limiting process [34]. In this study, it is shown in Fig. 6 that the plot of q_t versus $t^{0.5}$ exhibited an initial linear portions followed by downward deviation which occurred after 60 min. The linear portions of the plots are probably attributed to the intraparticle diffusion, the initial downward deviation of the plots seems to be due to boundary layer adsorption whereas the plateau corresponds to the equilibrium. Although the linear plots passed through the origin, downward deviation existed in each plot

Fig. 3. Kinetic isotherms of oxamyl adsorption at 298 K. **Fig. 4.** Application of pseudo-first order rate equation to oxamyl adsorption data at 77 K. **Fig. 5.** Application of pseudo-second order rate equation to oxamyl adsorption data at 77 K.

Table 3. Langmuir constants of oxamyl adsorption onto the activated carbons

Carbon	Adsorption temperature (K)							
	298		305		313		318	
	q_m	b	q_m	b	q_m	b	q_m	b
	mg/g	L/g	mg/g	L/g	mg/g	L/g	mg/g	L/g
CS 17	5.9	1.01	5.5	1.05	5.0	1.11	4.4	1.16
CS 32	15.9	1.01	14.5	1.03	13.2	1.05	12.1	1.08
CS 49	16.7	1.41	15.0	1.47	13.8	1.50	13.0	1.53
CS 65	15.2	1.01	14.0	1.12	12.9	1.28	12.1	1.45

Table 4. The thermodynamic parameters of oxamyl adsorption by the activated carbons

Carbon	Adsorption temperature (K)								
	298		305		313		318		$-\Delta H^\circ$
	$-\Delta G^\circ$	$-\Delta S^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$	
	KJ mol ⁻¹	J mol ⁻¹ K ⁻¹	KJ mol ⁻¹	J mol ⁻¹ K ⁻¹	KJ mol ⁻¹	J mol ⁻¹ K ⁻¹	KJ mol ⁻¹	J mol ⁻¹ K ⁻¹	
CS 17	0.085	49.0	0.127	48	0.270	40	0.391	45	14.7
CS 32	0.025	10.0	0.076	10	0.130	9	0.211	9	3.05
CS 49	0.85	8.0	0.98	7	1.05	7	1.12	6.6	3.23
CS 65	0.025	43	0.29	41	0.65	39	0.98	31	12.75

which stands for boundary layer adsorption. This particular type of adsorption seems to be too small to control the adsorption process. The correlation coefficients for intra-particle diffusion model (R_p^2) were 0.9995, 0.9990, 0.9992 and 0.9971 for CS17, CS32, CS49 and CS65, respectively. These values indicate that the adsorption of the oxamyl onto activated carbons investigated may be followed by intra-

particle diffusion up to 60 min.

3.4. Adsorption equilibrium

The adsorption isotherm is important for describing the interaction of the solute with the sorbent which is critical in optimizing the use of the latter. In addition, the adsorption of solvated charged species and oriented dipoles existing at the activated carbon-electrolyte interface may be predicted by the adsorption behavior at different concentrations.

Figure 7, shows the oxamyl adsorption isotherms onto ACs investigated undertaken at 298 K. The isotherms are typical type L according to Giles classification [35]. The adsorption data of oxamyl adsorption onto the ACs at 298, 305, 313 and 318 K were analyzed using the widely used Langmuir equation [36]. The linear form of this equation may be represented as follows:

$$\frac{1}{q_e} = \left(\frac{1}{b \cdot q_m} \right) \frac{1}{C_e} + \frac{1}{q_m} \quad (4)$$

Where q_e is the amount adsorbed (mg/g) at an equilibrium concentration C_e (g/L), q_m (mg/g) is the amount adsorbed corresponding to a complete monolayer coverage and b (L/g) is known as Langmuir constant which can be used to determine the free energy change of the adsorption process using the relationship.

$$\ln \frac{1}{b} = \frac{\Delta G^\circ}{RT} \text{ or } \Delta G = -RT \ln b \quad (5)$$

When the adsorption was carried out at different temperatures the enthalpy change ΔH could be calculated by plotting $\ln b$ versus $1/T$ with the slope of this linear plot determining ΔH . Consequently the entropy change ΔS° could

Fig. 6. Intraparticle diffusion plots for the adsorption of oxamyl at 298 K onto the activated carbon. **Fig. 7.** Adsorption isotherms of oxamyl at 298 K onto ACs.

Fig. 8. Linear Langmuir plots of axamyl adsorption onto ACs at different Temperatures (T1=298, T2=305, T3=313, T4=318 K).

Fig. 9. $\ln b$ versus $1000/T$ (K^{-1}) for the investigated ACs.

be calculated from the relationship.

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \quad (6)$$

The linear Langmuir plots of oxamyl adsorption at 298, 305, 313 and 318 K are shown in Fig. 8. Excellent linear plots are shown with considerably high values of correlation coefficient R^2 . Evidently, the monolayer capacities of samples CS32, CS49 and CS65 are comparable whereas that of CS17 is by far lower. This may be attributed to the different textural properties of the latter. This point will be

discussed shortly.

The values of $\ln b$ versus $1/T$ are presented in Fig. 9. Satisfactory, straight line is shown. The values of ΔH° were calculated and are listed in Table 4. Included also in this table are the values of ΔG° and ΔS° .

Table 4 reveals that: although the values of ΔG° are relatively small, but they are all negative indicating that the adsorption of oxamyl by the ACs investigated in the temperature range 298-318 K, is thermodynamically feasible. The negative values of ΔH° indicate that the present adsorption process is a spontaneous process and the values

Fig. 10. q_m at 298 K versus S_n^a for the investigated ACs.

of ΔH refer to a physical adsorption process. The negative values of ΔS refer to the stability of the adsorption complex formed.

It remains now to point out that trials has been made to relate the adsorption capacities of the ACs for oxamyl to their textural parameters of the ACs listed in Table 1, one can simply exclude the total surface area S_{BET} for example, q_m of CS65 is about 2.6 time larger than that of CS17 although both exhibit comparable S_{BET} values. The total pore volume V_T may be also excluded for example, q_m measured value is smaller than that of CS32 although exhibiting higher V_T than that of CS32. The successful trial was found when was related to the surface area located in non-micropores S_n^a . Fig. 10 depicts q_m versus S_n^a . Evidently, a straight line represented the relationship between q_m and S_n^a . Moreover, this straight line passes through the origin which indicates that the surface located in non-micropores is the prominent factor in determining oxamyl adsorption. Oxamyl is a relatively bulky molecule inaccessible to adsorption in micropores. However, within the mesoporous range, i.e. for pores with $r_m > 1.0$ nm, oxamyl adsorption proved to be independent on the value of r_m .

4. Conclusions

The textural properties of steam-activated carbons depend on the percentage burn-off. The initial stage of gasification of a carbonization product with steam creates new micropores. Increasing of % burn-off widens the pore dimensions via pore walls erosion. Kinetic adsorption of oxamyl by ACs proceeded via pseudo-second-order model, the kinetic adsorption data were more applicable to this model compared with pseudo-first-order model. Adsorption capacities (q_m values) higher than 15 mg/g were calculated by applying the conventional Langmuir model to oxamyl adsorption by some activated carbons. The free energy change of oxamyl adsorption by ACs depicted the feasibility of the adsorption process. The small negative H_o values referred to the spontaneous physical adsorption and the entropy change indicated the stability of the adsorption

complex formed. The adsorption capacity of an activated carbon towards oxamyl may be controlled by the surface area located in non-micropores.

Reference

- [1] Balley, G. W.; White, J.L. *Residue Rev.* **1970**, 32, 29.
- [2] Mortland, M. M. *Adv. Agron.* **1970**, 22, 75.
- [3] Gertsl, Z. *Pestic* **1984**, 15, 9.
- [4] Cohen, S. Z.; Greeger, S. M.; Carsel, R. F.; Endield, G. G. ACS symp. Ser. Am. Chem. Soc. Washington. DC. USA 1984.
- [5] Rothschild, R. E.; Manser, R. J.; Anderson, M. P. *Ground Water* **1982**, 20, 437.
- [6] Bansal, O. P.; Gupta, V. J. *Indian Soil Sci* **1998**, 46, 36.
- [7] Alaya, M. N.; Hourieh, M. R.; Youssef, A. M.; EL-Sejarieh, F. *Adsorp. Sci. Technol.* **2000**, 18, 27.
- [8] El- Nabarawy, Th.; El- Hakam, S. A.; Youssef, A. M. *Adsorp. Sci. Technol.* **1996**, 13, 509.
- [9] Khalil, L. B. *Adsorp. Sci. Technol.* **1996**, 13, 317.
- [10] Li, D.; Scala, A. A.; Ma, Y. H. *Adsorption* **1996**, 2, 227.
- [11] Marshall, W. E.; Johns, M. M. J. *Chem. Technol. Biotechnol.* **1996**, 66, 192.
- [12] Youssef, A. M.; El- Khouly, A. I.; Ahmed, A. I.; EL-Shafey, E. I. *adsorp. Sci. Technol.* **1995**, 12, 211.
- [13] Youssef, A. M.; Abdl-Bary, E. M.; Samra, S. E; Dawidar, A. M. J. *Polym. Sci.* **1994**, 55, 97.
- [14] McKay, G.; El- Geundi, M.; Nassar, M.M. *Adsorp. Sci. Technol.* **1997**, 15, 737.
- [15] Gaikar, V. G.; Mandal, T. K.; Kulkarni, R. G. *Sep. Sci. Technol.* **1996**, 31, 259.
- [16] Hasany, S. M.; Ahmad, R. *Main Group Met. Chem* **2003**, 26, 87.
- [17] McKay, G.; Vong, B.; Porter, J.F. *Adsorp. Sci. Technol.* **1998**, 16, 51.
- [18] Weber, Jr. W. G.; "Adsorption Technology", Slejke, FL., Ed, Marcel Dekker, New York/ Basel, M.N. **1985**, 399.
- [19] Alaya, M. N.; Youssef, A. M.; Karman, M.; Abdel-AL, H.E. *Carbon Science.* **2006**, 7, 9.
- [20] Strelko, V. Jr.; Malik, D. J. J. *Colloid Interface Sci.* **2000**, 250, 213.
- [21] Youssef, A. M.; Ahmed, A. I. 15th Biennial conference on carbon, Philadelphia USA 1981, p. 253.
- [22] Rodriguez-Reinaso, F.; Rodriguez-Rames, I., Guerrero-Ruiz, A.; Lopez- Gonzalaz, D. *Appl. Catal.* **1986**, 21, 257.
- [23] Strelko, Vladimir, Jr.; Malik Danish, J. J. *Coll. and Interf. Sci.* **2000**, 213.
- [24] Hourieh, M. A.; Alaya, M. N.; Youssef, A.M.; El-Sejarieh, F. *Adsorp. Sci. Technol.* **1999**, 17, 675.
- [25] Youssef, A. M., Radwan, N. R. E.; Abdel-Gawad, I.; Singer, G. A. A. *Colloids and Surfaces.* **2005**, 252, 143.
- [26] Singhal, J. P.; Khan, S. U.; Bansal, O. P. J. *Agric. Food. Chem.* **1977**, 25, 377.

- [27] Brunauer, S. Deming, L. S.; Deming, W. S.; Teller, E., *J. Am. Chem. Soc.* **1940**, 62, 1723.
- [28] Brunauer, S.; Emmett, P. H.; Teller, E., *J. Am. Chem. Soc.* **1938**, 60, 309.
- [29] Sing, K. S. W. "Surface Area Determination, Proc. Int. Symp., 1970, Bristol, Butterworths, London, UK, P .25.
- [30] Maria Jesus S. P.; Jose M. M. J. *Chem. Soc. Faraday Trans.* **1991**, 87, 1237.
- [31] Kannan, N.; Sundaram, M. M. *Dyes Pigm.* **2001**, 51, 25.
- [32] Ho, Y. S.; Wase, D. A. J.; Forster, C. F. *Environ Techol.* **1996**, 17, 71.
- [33] Weber, Jr. W. J; Morris, Jr., J. C. *J. Saint Eng. Div., Am. Soc., Civil. Eng.* **1963**, 89, 31.
- [34] Khattri, S. D.; Singh, M. K. *Adsorp. Sci. Technol.* **1999**, 17, 269.
- [35] Giles, C. H.; MacEwan, T. H., Proc. 2nd Congr. Surface Activity, London **1959**, 457.
- [36] Panday, K. K.; Prasod, G; Singth, U. N., *Water Res.* **1959**, 19, 869.