Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Applied Science Research, 2012, 4 (2):1053-1060
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Statistical optimization for the prediction of ibuprofen adsorption capacity by using microwave assisted activated carbon

Monal Dutta, Pinaki Ghosh and Jayanta Kumar Basu*

Indian Institute of Technology, Kharagpur, Kharagpur, India

ABSTRACT

The adsorption of ibuprofen was optimized by response surface methodology (RSM) through a three level Box-Behnken design (BBD). The microwave assisted activated carbon derived from scrap wood of Acacia Auriculiformis was used as an adsorbent for the present study. The optimization through RSM involves the approximation of several independent dependent variables. In the present scenario solution pH, initial adsorbate concentration, adsorbent dose, contact time and reaction temperature were considered as the input variables whereas, the ibuprofen adsorption capacity was chosen as the response variable. The quadratic model was suggested to predict the ibuprofen removal efficiency. From the analysis of variance (ANOVA) it was found that solution pH, adsorbent dose, contact time and reaction temperature had significant effects on ibuprofen adsorption. With help of numerical optimization technique the adsorption process was optimized and a good desirability value (1.0) was also obtained. The experimental and model predicted values of the ibuprofen adsorption were compared and both the values were found to be in reasonable agreement with each other.

Keywords: Response surface methodology, Box-Behnken, desirability value, analysis of variance, numerical optimization.

INTRODUCTION

Ibuprofen is widely known as an analgesic drug especially used for inflammation and dysmenorrhea. It is also used in the treatment of arthritis. Ibuprofen is known to have an antiplatelet effect, though it is relatively mild and somewhat short-lived when compared with aspirin or other better-known antiplatelet drugs [1]. In general, ibuprofen also acts as a vasodilator, having shown the capability to dilate coronary arteries and some other blood vessels. Ibuprofen is designated as a core medicine in the "WHO Model List of Essential Medicines". Ibuprofen is generally derived from propanoic acid [2]. Along with wide variety of medical applications ibuprofen has some adverse effects on human body including nausea, dyspepsia, gastrointestinal ulceration/bleeding, raised liver enzymes, diarrhea, constipation,epistaxis, headache, dizziness, priapism, rash, salt and fluid retention, and hearing loss [3]. So far, very little has been known about the synergistic and long-term effects of continuous exposure to this drug, even if it is present in a very trace amount [4]. But, the pollution caused by ibuprofen is very difficult to control and they could be very detrimental to aquatic life if they enter into the water stream [5, 6]. Therefore removal of ibuprofen from the waste stream has become very important. Various commercial techniques such as, chemical oxidation [7], coagulation and floatation [8], biodegradation, adsorption [9], photocatalysis [10], ion exchange [11] and membrane separation [12] are available for the removal of these substances but adsorption process is the worth mentioning among all of them [13]. In most of the cases, the adsorption of pollutants is carried

out by using commercial activated carbon [14]. However, its higher cost limits its widespread uses. But implementation of a low-cost adsorbent does not serve all economic cornerstones in case of a large scale process. In such a situation use of furniture wood scraps as a precursor of activated carbon could be a better alternative [15, 16, 17]. On the other hand, the removal of ibuprofen can be optimized through response surface methodology (RSM). The response surface methodology (RSM) is a statistical design procedure which optimises a process by correlating the process variables through regression analysis [18]. According to the previous literature efforts have been made to separate ibuprofen from its aqueous solution by using different activated carbons prepared from cork waste [19], municipal waste [20], biological activated carbon [21] but no effort was made so far to optimize the ibuprofen adsorption process through response surface methodology where microwave assisted activated carbon was used as an adsorbent. Therefore, in the present investigation the adsorption of ibuprofen by using microwave activated carbon was studied. The adsorption process was optimized by using response surface methodology through a three level Box-behnken design (BBD).

MATERIALS AND METHODS

2.1 Materials

The scrap wood of Acacia Auriculiformis was collected from local saw mill of Kharagpur. Ibuprofen was supplied by Shivlal and Company, Kolkata. Hydrochloric acid and ammonia were procured from Merck Specialities Private Limited, Mumbai, India.

2.2 Preparation of the activated carbon

The wood scraps were first cut into small pieces of 2 mm width and 40 mm of length, cleaned with distilled water and was sun dried for 24 h prior to the carbonization process. The wood pieces were kept on a ceramic boat which was placed at the center of a 40-mm i.d tubular furnace. The material was then heated from ambient temperature to the carbonization temperature of 750 °C at the rate of 4 °C/min in a continuous flow of N_2 (300 ml/min) and then it was kept at this temperature for 1h for subsequent activation. The product was then allowed to cool to ambient temperature in presence of N_2 flow and sieved to obtain the desired size fractions. It was further stored in a desiccator over silica gel. The char prepared in this way is termed as C750N. The C750N was further activated in a domestic microoven (IF20PG3S) for five minutes at a constant input power of 800 W and a frequency of 2450 MHz. After treating in the microoven C750N was termed as AC750NMW5.

2.3 Characterization of activated carbon

The surface area and the total pore volume of the prepared char and the activated carbons were determined by using N_2 adsorption-desorption method by using Brunauer Emmett Teller (BET) apparatus (Autosorb-1, Quantacrome). The surface properties and the microporous structure were investigated by using Scanning Electron Microscope (SEM) (Hitachi, model SU-70). The total ash content and the apparent density of the prepared char were also determined.

2.4 Batch adsorption study

The batch adsorption study was carried out in a mechanical shaker at varying experimental conditions. For this purpose, 100 ml ibuprofen stock solutions of varying concentrations were taken in a series of 250 ml volumetric flasks and placed inside the shaker after adding the weighted amount of adsorbent into it. An aliquot of the sample was taken out at a predetermined time interval and analyzed in a UV-Vis spectrophotometer. The adsorption capacity was calculated from the relationship:

$$q_t = \frac{(C_0 - C_t)}{w} V \qquad (1)$$

Where, q_t (mg/g) is the adsorption capacity, C_t is the ibuprofen concentration at any time t (mg/l/), V is the volume of solution (l) and w is the weight of adsorbent (g).

2.5. Statistical modeling and process optimization by Box behnken design

The ibuprofen adsorption process was successfully optimized by using a three level Box behnken design (BBD). In the present investigation solution pH (x_1), initial adsorbate concentration (x_2), adsorbent dose (x_3), contact time (x_4) and reaction temperature (x_5) were considered as the input variables whereas, the ibuprofen adsorption capacity Y_1

(mg/g) was chosen as the response variable. The input and the response variables can be correlated by using the following polynomial equation.

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (2)$$

where, Y is the response and β_0, β_i, β_{ii}, β_{ij} are the coefficients of the intercept, linear, square and interaction effects respectively. The regression model was statistically analyzed by using Design expert software (Stat-Ease, Inc., version 8.0.7.1, Minneapolis, USA). The range and levels of the input variables are shown in Table 1.

Table 1: The experimental range and levels of the input variables

Input variables	Range (+1)	Range (-1)
Solution pH (x_1)	2	8
Initial concentration, mg/l (x_2)	30	60
Adsorbent dose, (mg/l) (x_3)	1	3
Contact time, (min) (x_4)	10	110
Reaction temperature, (°C) (x_4)	10	50

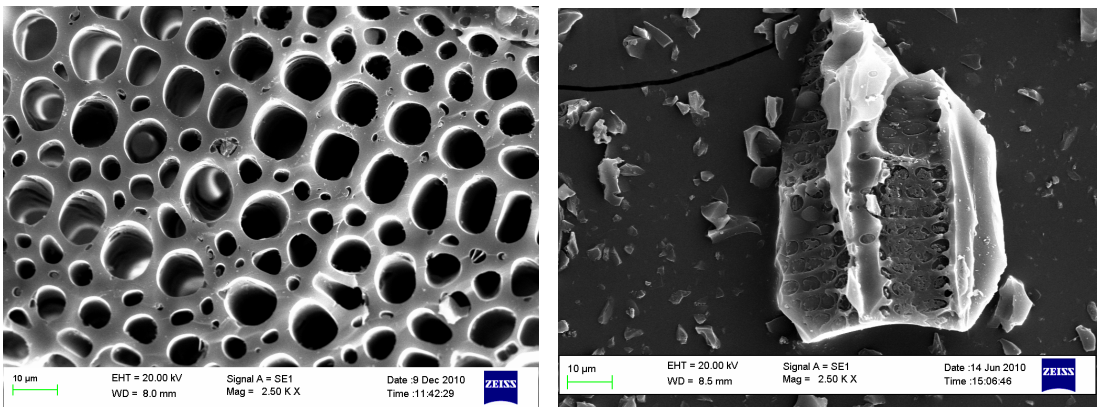
RESULTS AND DISCUSSION

3.1 Comparison of surface properties of activated carbons

The BET surface area (S_{BET}), total pore volume (V_{tot}) and average pore size of C750N, and AC750NMW5 were determined from the physical adsorption data of N_2 at 77 K and the values are shown in Table 2. It was seen from Table 2 that AC750NMW5 had the highest surface area and total pore volume. Inside the microoven a high temperature could be reached in comparatively shorter period of time resulting in dissipation of huge amount of energy at a molecular level. Consequently, the roughness of the pore walls may also be increased due to rapid heating with the formation of additional active sites [22]. Besides, rapid heating could accelerate the release of tar or volatile matter from the pore interior which results into higher pore volume [23].

Table-2: Comparison of surface properties of different adsorbents

Adsorbent	Surface area (m^2/g)	Total pore volume (cc/g)	Average pore diameter (Å)
C750N	514.2	0.36	27.99
AC750NMW5	54695	0.50	28.55



(a) **(b)**

Fig. 1. The SEM image of (a) C750N (b) AC750NMW5

3.2 Surface morphology of activated carbons

The surface morphology of activated carbons was investigated through Scanning electron microscope (SEM) analysis. The SEM images of various activated carbons are shown in Figure 1a – 1b. It was observed from Figure 1a that a typical honeycomb structure with pores of different sizes was formed on the surface of char (C750N) when it

was treated at optimum condition. The similar surface morphology could also be observed when activated carbon was prepared from corncob by chemical activation [24]. The roughness of the interior pores of activated carbon was further increased by treating it in a domestic microoven (Figure 1b).

3.3. The model equations and analysis of variance (ANOVA)

In the present scenario, quadratic model was suggested by the proposed Box-Behnken design to predict the ibuprofen adsorption capacity. The complete design matrix was consisted of forty six experimental runs with six replicates at the center points. The quadratic model equations corelating the input and output variables were given as follows:

$$Y_1 = 17.59 - 3.42x_1 + 1.25\ x_2 - 10.87\ x_3 + 1.68\ x_4 - 1.40\ x_5 - 2.66\ x_1\ x_2 + 0.26\ x_1\ x_3 - 0.81\ x_1\ x_4 - 1.95\ x_1\ x_5 - 2.63\ x_2\ x_3 + 1.23\ x_2\ x_4 - 0.20\ x_2\ x_5 + 0.87\ x_3\ x_4 + 0.19\ x_3\ x_5 - 0.35\ x_4\ x_5 - 0.89x_1^2 - 1.31x_2^2 + 5.93x_3^2 - 1.52x_4^2 - 2.46x_5^2 \quad (3)$$

The adequacy of the models was justified by the analysis of variance (ANOVA). The ANOVA of ibuprofen adsorption capacity q_t (mg/g) is given in Table 3. The model F-value is the ratio of mean square for the individual term to the mean square for the residual. The Prob > F value is the probability of f-statistics value and is used to test the null hypothesis. The parameters having an F-statistics probability value less than 0.05 are said to be significant. In the present study, x_1, x_3, x_4, x_5, x_1x_2, x_2x_3, x_3^2, x_5^2 were designated as significant model terms. Therefore it can be concluded that the solution pH, adsorbent dose, contact time and reaction temperature play an important role in case of ibuprofen adsorption. The similar result was also obtained by Mestre et. al., where the adsorption of ibuprofen was studied by using waste derived activated carbon. Here also the solution pH had a significant effect on ibuprofen adsorption. Once the optimization was over the experimental and model predicted values of the response variable were compared. The plot between experimental (actual) and predicted values of ibuprofen adsorption capacity q_t (mg/g) is shown in Fig. 2. It can be seen from Fig. 2 that both the values were in reasonable agreement with each other. It implied that a good correlation between input and output variables could be drawn by the model developed.

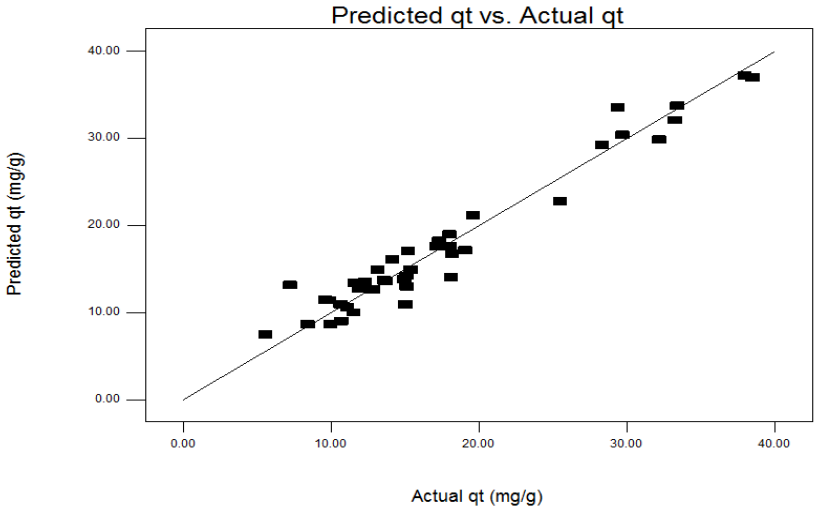


Fig 2. The plot of predicted versus actual values for ibuprofen adsorption capacity

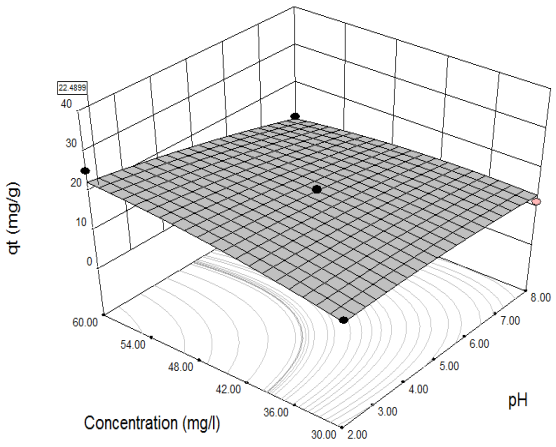
3.4. Effects of experimental parameters on ibuprofen adsorption

The effects of various experimental parameters such as solution pH, initial concentration, adsorbent dose, contact time and reaction temperature on the ibuprofen adsorption is shown in Fig.3a – 3d. It was seen from Fig. 3a- 3d that the ibuprofen adsorption capacity was increased with increase in initial concentration, contact time and decrease in solution pH, adsorbent dose and temperature. The adsorption of ibuprofen favors at comparatively lower pH values (Fig. 3a). As ibuprofen is known to be a weak electrolyte, ionization of ibuprofen molecule strongly depends upon the solution pH. At lower solution pH the neutral molecule represents the main structure but as the solution pH is further increased the ibuprofen molecules starts converting to some other molecule which results into lower adsorption capacity [26]. The combined effect of initial concentration and adsorbent dose on the adsorption of ibuprofen is presented in Fig. 3b. As the adsorbate concentration increases the concentration gradient which acts as

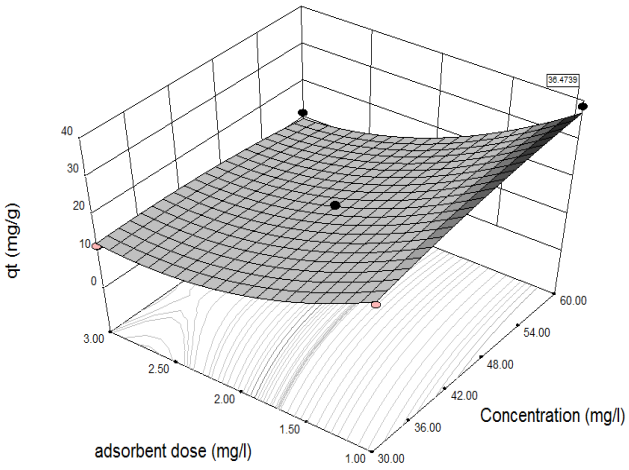
the main driving force for mass transfer also increases which in turn results into higher adsorption capacity [27]. It was further noticed from Fig. 3b that the maximum adsorption capacity of 36.47 mg/g was obtained with an adsorbent dose and initial concentration of 1 g/l and 55 mg/l respectively. On the other hand the effect of contact time and reaction temperature on ibuprofen adsorption can be seen from Fig. 3c. As the time progresses more and more ibuprofen molecules get attached on the activated carbon surface thus enabling higher ibuprofen adsorption capacity [28]. The adsorption capacity of ibuprofen was increased with decrease in reaction temperature (Fig. 3d). This phenomenon represents the exothermic nature of the adsorption process [29].

Table 3: Analysis of variance for ibuprofen adsorption capacity q_t (mg/g)

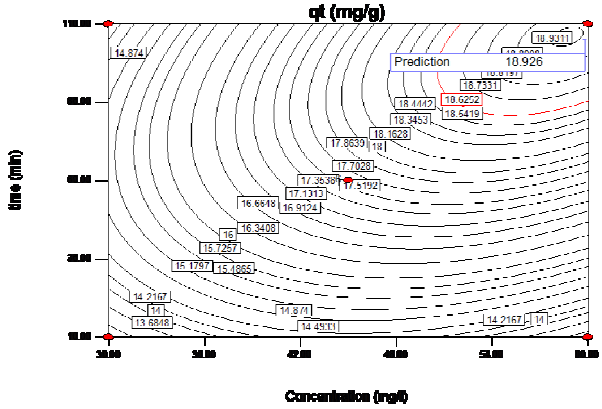
Source	Sum of Squares	df	Mean Square	F Value	Prob > F
x_1	186.75	1	186.75	29.99	< 0.0001
x_2	25.04	1	25.04	4.02	0.0558
x_3	1889.49	1	1889.49	303.45	< 0.0001
x_4	45.17	1	45.17	7.26	0.0124
x_5	31.36	1	31.36	5.04	0.0339
x_1x_2	28.26	1	28.26	4.54	0.0432
x_1x_3	0.28	1	0.28	0.045	0.8339
x_1x_4	2.63	1	2.63	0.42	0.5214
x_1x_5	15.24	1	15.24	2.45	0.1303
x_2x_3	27.70	1	27.70	4.45	0.0451
x_2x_4	6.03	1	6.03	0.97	0.3344
x_2x_5	0.16	1	0.16	0.025	0.8756
x_3x_4	3.00	1	3.00	0.48	0.4940
x_3x_5	0.14	1	0.14	0.023	0.8803
x_4x_5	0.49	1	0.49	0.079	0.7809
x_1^2	6.98	1	6.98	1.12	0.2997
x_2^2	14.90	1	14.90	2.39	0.1345
x_3^2	307.37	1	307.37	49.36	< 0.0001
x_4^2	20.25	1	20.25	3.25	0.0834
x_5^2	52.72	1	52.72	8.47	0.0075



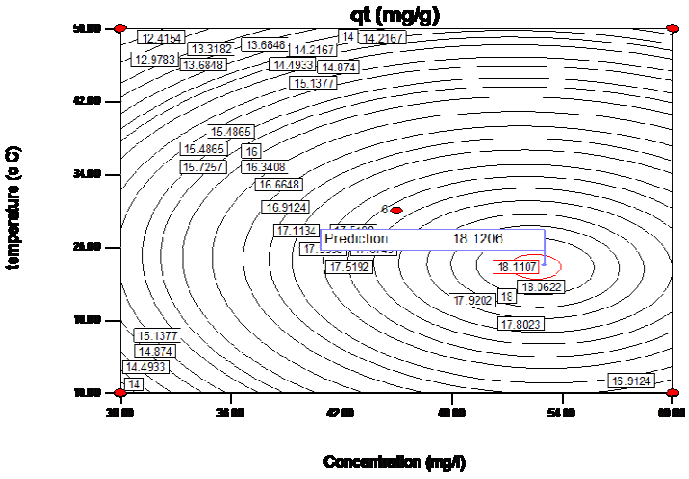
(a)



(b)



(c)



(d)

Fig. 4. The effects of (a) solution pH and initial adsorbate concentration (b) adsorbent dose and initial adsorbate concentration (c) contact time and initial adsorbate concentration (d) temperature and initial concentration on the adsorption of ibuprofen

4.7. Optimization of process variables

The numerical optimization was applied to optimize the ibuprofen adsorption process and the optimum values of various parameters are provided in Table 4. A desirability value of 1.0 was obtained after optimizing the process parameters.

Table 4: The optimum values of the experimental parameters

Parameters	Optimum values
Solution pH	2
Initial concentration (mg/l)	60
Adsorbent dose (g/l)	1
Contact time (min)	110
Reaction temperature (° C)	10.84

CONCLUSION

The adsorption of ibuprofen was carried out by using micro-wave activated carbon. The adsorption process was successfully optimized by using Box-Behnken design. The solution pH, initial adsorbate concentration, adsorbent dose, contact time and reaction temperature were selected as the input variable for the Box-Behnken design whereas, the ibuprofen adsorption capacity was considered as the response variable. The quadratic model was suggested by the software for the response variable. The experimental and predicted ibuprofen adsorption capacity values were compared and both of these values were found to be in well agreement with each other.

REFERENCES

[1] AV Esch, HAV Steensel-Moll, EW Steyerberg, M Offringa, JD habbema, G Derksen-Lubsen, *Arch. Ped. Adol. Med*., **1995**, 149,6, 632-637
[2] WHO Model List of Essential Medicines for Children, 2nd ed., MIMS Australia
(UBM Medica Australia Pty Ltd, Australia, **2010**.
[3] SG Curhan, R. Eavey; J Shargorodsky; GC Curhan, *Am. .J.Med.*, **2010**, 123, *3*, 231–237.
[4] D Barcelo. *Trends Anal. Chem*., **2003**, 22, *10*, 14-16.
[5] OA Jones; JN Lester; N Voulvoulis, *Trends Biotechnol*, **2002**, 23, 163–167.
[6] MJ Gomez; MJ Martinez-Bueno; S Lacorte; AR Fernandez-Alba; A Aguera, *Chemosphere*, **2007**, 66, 993–1002.
[7] PK Malik; SK Saha, *Sep. Purif. Technol*., **2003**, 31, 241–250.
[8] J Panswed; S Wongchaisuwan, *Wat. Sci. Technol*., **1986**, 18, *3*, 139–144.
[9] V Lopez-Grimau; MC Gutierrez, *Chemosphere*, **2006**, 62, 106–112.
[10] SS Tahir; N Rauf, *Chemosphere*, **2006,** 63, 1842–1848.
[11] JX Chen; LH Zhu, *Chemosphere*, **2006**, 65, 1249–1255.
[12] G Ciardelli; L Corsi; M Marucci, *Resour. Conserv. Recycl*., **2000**, 31, *2*, 189–197.
[13] FC Wu; RL Tseng, *J. Hazard. Mat*., **2006**, 152, *3*, 1256–1267.
[14] WW Eckenfelder Jr. Ind. Wat. Poll. Cont., 3rd ed., McGraw-Hill, NewYork, **1966**.
[15] S Karagöz; T Tay; S Ucar; M Erdem, *Bioresour. Technol*., **2008**, 99, 6214–6222.
[16] C Michailof; GG Stavropoulos; C Panayiotou, *Bioresour. Technol*., **2008**, 99, 6400–6408.
[17] SY Wang; MH Tsai; SF Lo; MJ Tsai, *Bioresour. Technol*., **2008**, 99, 7027–7033.
[18] J Lee; L Ye; WO Landen Jr.; RR Eitenmiller, *J. Food Comp.Anal.*, **2000**, 13, *1*, 45–57.
[19] AS Mestre; J Pires; JMF Nogueira; JB Parra; AP Carvalho; CO Ania, *Bioresour. Technol.*, **2009**, 100, 1720–1726.
[20] AS Mestre; J Pires; JMF Nogueira; AP Carvalho, *Carbon*, **2007**, 45, 1979–1988.
[21] W Nugroho; J Reungoat; J Keller, *J. Appl. Sci. Environ. Sanit*., **2010**, 5, *2*, 131-141.
[22] L Huang; Y Sun; W Wang; Q Yue; T Yanga, *Chem. Eng. J.*,**2011**, 171,*3*, 1446-1453.
[23] QS Liu; T Zheng, P Wang; L Guo, *Ind. Crop. Prod.*, **2010**, 31, 233–238.
[24] RL Tseng. *J. Coll. Interf. Sci*., **2006**, 303, *2*, 494–502.
[25] AS Mestre; J Pires; JMF Nogueira; JB Parra; AP Carvalho; OA Conchi, *Bioresour.Technol*., **2009**, 100, 1720–1726.
[26] N Lindqcist; T Tuhkanen; L Kronberg, *Wat. Res*., **2005**, 39, 2219–2228.
[27] AS Mestre; J Pires; JMF Nogueira; AP Carvalho, *Carbon*, **2007**, 45, 1979–1988.
[28] W. Nugroho, J Reungoat, J Keller, *J. Appl. Sci. Environ. Sanit., 5 (2): 131-141.*

[29] YS Al-Degs, MI El-Barghouthi, AH El-Sheikh, GM Walker, *Dyes Pigm*., xx, 1-8, **2007**.