Adsorption of Auramine-O Using Activated Globe Artichoke Leaves: Kinetic and Isotherm Studies

Laribi Kahina[1,*] and Sahmoune Mohamed Nasser[1,2]

[1]Laboratory of Soft Technologies and Biodiversity, Faculty of Sciences, University M'hamed Bougara of Boumerdes, Boumerdes 35000, Algeria

[2]Environnement Genius Departement, Faculty of Sciences of the Engineering, University of Boumerdes, Boumerdes 35000, Algéria

*Corresponding author: l.kah@hotmail.fr

The aim of this work was to study the removal of auramine-O (Au-O) from aqueous solution using powder prepared from globe artichoke leaves chemically activated with NaOH solution. The physico-chemical characteristics of the samples were performed and the characterization by FT-IR analysis has been carried out to examine the structure of globe artichoke leaves before and after activation. Scanning electron microscope was used to analyze the surface change of the globe artichoke leaves before and after adsorption of dye solution. A comparison of two models on the overall adsorption rate showed that the kinetic of adsorption was better described by the pseudo-second order model. The equilibrium data fitted very well to Langmuir model with maximum monolayer adsorption capacity of 344.8 mg g^{-1} at 298 K. This study shows that the globe artichoke leaves can be used as low cost alternative adsorbent for removal of auramine-O.

Keywords: Globe artichoke leaves, auramine-O, Adsorption, Kinetics.

INTRODUCTION

The wastewater contains a variety of compounds organic matter and toxic substances harmful to fish and other aquatic organisms [1,2]. Various dyes used in textile industry cause serious problems, because of their stability and low biodegradability [3,4] and there elimination has been the subject of much attention in recent years, not only because of their toxicity, but mainly because of their detection problems [5-8]. Various physico-chemical and biological processes have been investigated to remove the dyes in wastewater [9,10]. Among the methods, removal of dyes by adsorption is regarded as one of the competitive methods because of high efficiency, economic feasibility and simplicity of design/operation [11-13]. The activated carbon is the most widely used for the removal of dyes and effluent treatment textile, because activated carbons are prepared from natural materials such as wood or coal, which are expensive [14-16]. Recently, low cost and easily available other agricultural based materials such as wheat shells, banana pith, maize cob [17,18], pistachio shells [19,20], date stones [21], date pits [22], seed stone [23], coir pith [24], rice husk [25,26], bagasse [27], straw [28], seeds waste [29], apricot stone [30], almond barks, coffee seeds, tea waste, rice husk *etc*. [31,32] have been used as a source of the production of activated carbon for the removal of the textile dye effluents. In this study we have utilized the globe artichoke leaves (GAL)

as an adsorbent to remove the basic dyes auramine-O (Au-O) in an aqueous solution. The equilibrium analyzes were conducted to understand the sorption processes.

EXPERIMENTAL

Adsorbate: The basic dye used is auramine-O($C_{17}H_{22}ClN_3$) solution. 1000 mg/L was prepared and from which dilutions were performed.

Adsorbent preparation: Globe artichoke leaves used for this study were obtained from Relizane, Algiers. The globe artichoke leaves were washed with distilled water, dried at 85 °C for 24 h and milled. 20 g of powder was mixed with 1 L of 0.1 M NaOH. The mixture is washed several times with distilled water until the pH became neutral. The sample was thereafter dried in an electric oven for 24 h at 95 °C and then kept in desiccators for use after crushing; the mean diameter of our samples is 620 μm.

Characterization of adsorbent: The surface area of the adsorbent was determined by the test at task (NF EN 933-9). The moisture content was determined according to standard method. Bulk density was determined using the method of Okieimen *et al.* [33]. The pH is determined according to (NF V 05-108, 1970) by immersing a 1 g sample in 100 mL of distilled water and stirring and heating for 1 h. The dosage of the surface features was performed by Boehm titration method

[6] to determine the quantities of the lactone function, phenolic, carboxylic and basic on fibers of activated artichoke.

In order to identify the main chemical functions present at the surface of the powdered globe artichoke leaves, infrared analysis was performed with a Fourier transform spectrometer JASCO Model 40100 for plotting spectra between 4000 and 400 cm⁻¹. The powder biomass microstructure was characterized by observation with a scanning electron microscope PHILIPS ESEMXL 30 tungsten filament coupled with a complete system of microanalysis EDSX.

Batch adsorption test: The adsorption experiments were carried out in a static reactor by introducing 0.1 g of adsorbent in 100 mL of a solution containing various amounts of auramine-O with intermittent stirring.

At the end of adsorption, the solutions were centrifuged and then subjected to quantitative analyses. For the kinetic and equilibrium studies, desired quantity of GAL is contacted with 100 mL of Au-O solutions in Erlenmeyer flasks. The flasks are placed on a rotary shaker at 250 rpm and the samples are taken at regular time intervals and centrifuged at 3000 rpm for 10 min. The Au-O contents in the supernatant was measured spectrophotometrically on Perkin Elmer UV-visible spectrophotometer model 550S at the λ_{max} value, which is 434 nm for auramine-O. The amount of auramine-O and the adsorption percentage were calculated using the following equations [34]:

$$q_e = V\,(C_0 - C_e)/m \tag{1}$$

$$R\,(\%) = (C_0 - C_e)/C_0 \times 100 \tag{2}$$

where, q_e (mg/g) is the amount adsorbed per gram of adsorbent; C_e (mg/L) is the equilibrium concentration of auramine-O, C_0 (mg/L) is the initial concentration of adsorbate; V (L) is volume of solution and m (g) is mass of adsorbent used.

Due to the inherent bias resulting from linearization of the isotherm and kinetic models, the non-linear regression root mean square error (RMSE) test is employed as criterion for the quality of fitting [13].

$$RMSE = \sqrt{\frac{1}{n-2}\sum_{1}^{n}(q_i - q_{ie})^2}$$

where, q_i (exp) (mg/g) is the experimental value of uptake, q_{ie} (cal) the calculated value of uptake using a model (mg/g) and n the number of observations in the experiment (the number of data points). The small the RMSE values, better the curve fitting [13].

RESULTS AND DISCUSSION

FTIR: Infrared spectra of the artichoke leaves before and after activation are almost identical. The IR spectra of artichoke leaves before activation are almost identical (Fig. 1). Localized at 3366.94 cm⁻¹ peak corresponds to OH group. While the bands at 2926.59–2333.55 cm⁻¹ reflect C-H bonds and CH₂, respectively, component of hemi-cellulose and cellulose [35] is over.

The band at 2109.83 cm⁻¹ is due to the OH bond by intramolecular hydrogen bonding. The absorption at 1740.51 cm⁻¹ band can be attributed to the carbonyl group (>C=O) stretching vibration of the bond in the lignin carboxylic acid or ester
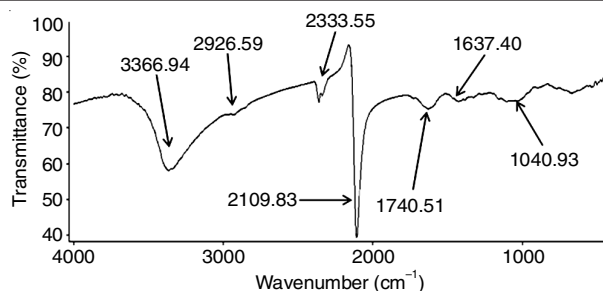

Fig. 1. FTIR spectra of activated globe artichoke leaves

group C=O in the hemicellulose [36]. The band at 1637.4 cm⁻¹ corresponds to C=O amide adsorption. The absorption at 1428 cm⁻¹ is associated with the symmetrical bending of CH₂ present in cellulose [37]. The two peaks observed at 1388.94 and 1332 cm⁻¹ are attributed to the bending vibration of CO and CH groups of polysaccharides aromatic ring [38]. The absorption peak centered at 1257.55 cm⁻¹ is due to the C-O bond stretching vibration of the acetyl group in lignin [39]. Both bands 1062.23 and 1040.93 cm⁻¹ may be associated, respectively, with the CO stretching modes of hydroxyl groups and the cellulose ether [35].

Scanning electron microscopy analysis: Fig. 2 shows the microstructure of artichoke leaves activated grain (Fig. 2A) and activated dye loaded (Fig. 2B).
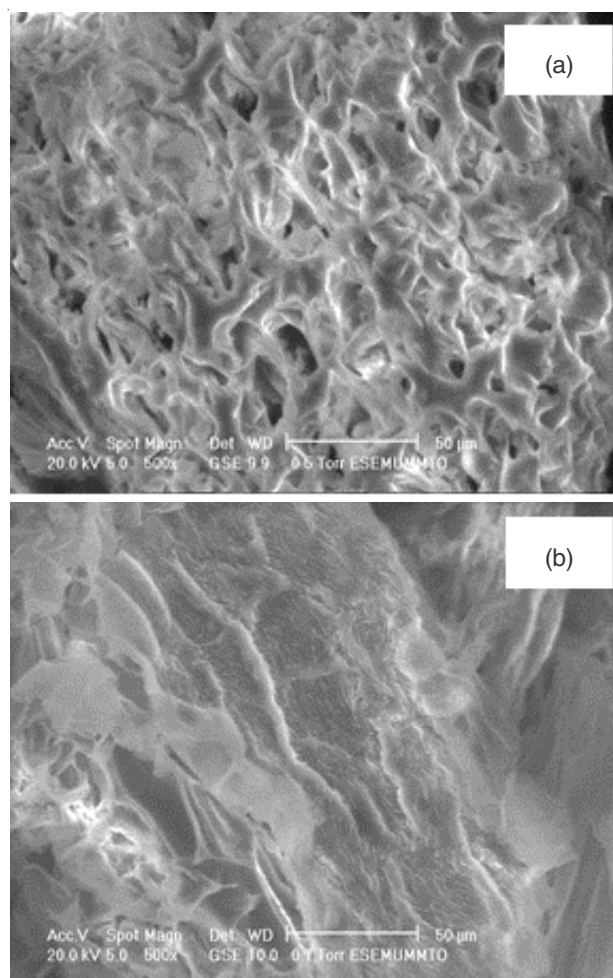

Fig. 2. SEM pictures of the biomass: Magnification × 1000 (a) activated biomass (NaOH 0.1 N) (b) activated biomass with dye

SEM pictures display morphology of GAL samples before and after the adsorption process. Fig. 2 showed that the GAL has numerous pores are the accessible sorption sites for dye uptake. That can allow a good diffusion of the dye and increase the number of accessible sites [40,41]. Fig. 2B showed that the pores are clogged after adsorption of Au-O on the support.

The results of physico-chemical analysis were represented in Table-1.

TABLE-1
CHARACTERISTICS OF ACTIVATED GLOBE
ARTICHOKE LEAVES WITH NaOH

Parameters	Values
Humidity (%)	0.3 ± 0.001
Density (g/cm^3)	0.32 ± 0.002
pH	7.15 ± 0.001
Ash content (%)	0.936 ± 0.001
Area surface (m^2/g)	722.64 ± 0.34
Lactone groups (mmol/g)	2.3
Phenolic groups (mmol/g)	3,85
Carboxylic groups (mmol/g)	3.7
Total acidity (mmol/g)	9.85
Total basicity (mmol/g)	2.82

Kinetic adsorption: The modeling of the adsorption kinetics of the Au-O is tested by two models:

Pseudo-first-order [42]:

$$\ln (q_e - q_t) = \ln q_e - k_1/2.303t \qquad (3)$$

where q_e and q_t are the quantities (mg g^{-1}) of the adsorbed Au-O at equilibrium at time t respectively and k_1 is the adsorption rate constant (mL min^{-1}). The constants of the model are determined graphically by plotting [ln (q$_e$-q$_t$)] as a function of t.

Pseudo-second-order [43]:

$$t/qt = 1/k_{2(}q_e)^2 + t/q_e \qquad (4)$$

where k_2 (g mg^{-1} min^{-1}) is the adsorption rate constant. The constants (k_2 and q_e) are also determined graphically by plotting (t/q$_t$) as a function of t.

The rate constants, predicted uptakes and the correlation coefficients for AGAL are summarized in Table-2. For the pseudo-second order kinetic, the experimental data approximate linearity.

TABLE-2
KINETIC PARAMETERS FOR ADSORPTION OF Au-O IONS
ONTO ACTIVATED GLOBE ARTICHOKE LEAVES WITH NaOH

	Model				
	Pseudo-first order		Pseudo-second order		
	q_e (mg g^{-1})	K_1 (g mg^{-1} min^{-1})	K_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	h (mg g^{-1} min^{-1})
	1.181	0.0011	14.92	18.41	22.7
R^2	0.1488		0.9997		
RMSE	5.289		0.647		

This was evidenced by the high values of q_e and correlation coefficients. Therefore, the pseudo-second order model is applicable to this system. The correlation coefficient and q_e, cal of the pseudo-second order kinetic model are in good agreement with the experimental results (Table-2).

The high value of correlation coefficient implies that Au-O adsorption on globe artichoke leaves may occur through a chemical process involving the valence forces of shared or exchanged electrons [44].

Adsorption isotherm: The adsorption isotherm is the relationship between the amount of an adsorbed substance at a constant temperature and its concentration in the solution at equilibrium. The literature describes two main models of adsorption isotherms. The Langmuir isotherm and Freundlich are the most frequently used models. In this study, the two models are used to analyze the relationship between the amount of dye adsorbed and its equilibrium concentration.

Langmuir isotherm: The Langmuir isotherm adsorption assumed that the adsorption takes place on homogeneous specific sites within the adsorbent and it has been used successfully for many adsorption in a monolayer process. The linearized Langmuir is represented by the following equation [45]:

$$1/q_e = 1/q_{max} + 1/bq_{max} C_e \qquad (4)$$

where C_e is the concentration of the adsorbent at equilibrium (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of the adsorbate (in mg/g) and Q and b are constants Langmuir.

The route of C_e/q_e depending this gives a straight line of slope $1/Q$ (Fig. 3), indicating that the adsorption of auramine-O onto AGAL does follow the Langmuir isotherm. 'b' and q Langmuir constants were evaluated from this isotherm and their values are recorded in Table-3, the Langmuir equation assumes that the surface is homogeneous. The important characteristics of the Langmuir isotherm can be expressed by a dimensionless parameter which is defined by R_L [46], which is defined by eqn. 5:

$$R_L = 1/(1 + bC_0) \qquad (5)$$

where C_o is the initial concentration of the higher solute, the constant b Langmuir adsorption (L/mg). The R_L value indicates the type of the isotherm: unfavourable ($R_L > 1$) linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L value obtained was 0.106. This confirms that the adsorbent made from artichoke leaves is very favourable for the adsorption of auramine-O under the conditions used in this work.

Freundlich isotherm: The Freundlich isotherm is an empirical equation used to describe heterogeneous systems. The logarithmic form the best known of the Freundlich model is given by the following equation [47]:
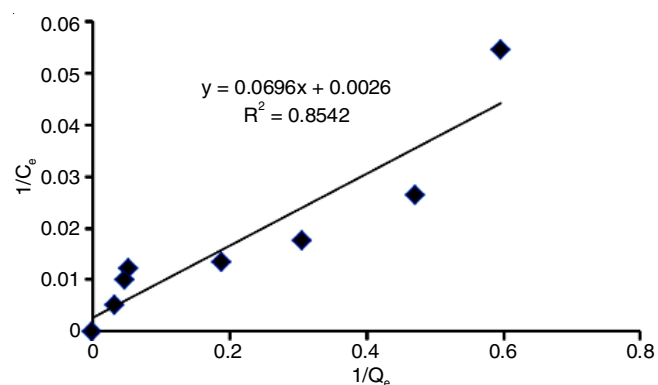

Fig. 3. Langmuir isotherm for the adsorption of auramine-O on AGAL (0.1 g/100 mL); [Au-O] 20 mg L^{-1}; T (298 K); Stirring (250 rpm); Stirring time (3 h)

TABLE-3
LANGMUIR AND FREUNDLICH ISOTHERM
CONSTANTS AT 298 K USING ACTIVATED
GLOBE ARTICHOKE LEAVES AS ADSORBENT

Langmuir isotherm			Freundlich isotherm	
q (mg/g)	b (L/mg)	R_L	k_F (mg/g) $(L/mg)^{1/n}$	1/n
344.8	0.042	0.106	7.063	1
R^2	0.8518		0.6346	
RMSE	22.863		104.076	

$$\log q_e = \log K_F + 1/n \log C_e \qquad (6)$$

where K_F and 1/n are constants related to the Freundlich adsorption capacity and the adsorption intensity of the adsorbent, respectively. q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate. The values of K_F and 1/n are calculated from the intercept and slope, respectively and are recorded in Table-3. The logarithm of the graph log q_e *versus* log C_e gives a straight line (Fig. 4) with a correlation coefficient of 0.8158.
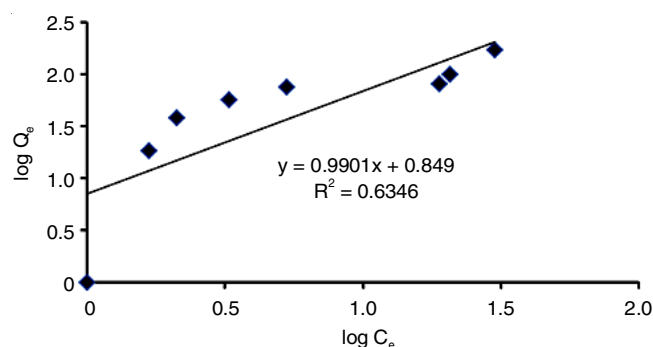

Fig. 4.　Freundlich isotherm for the adsorption of auramine-O onto AGAL 0.1 g/100 mL; [Au-O] 20 mg L^{-1}; T (298 K); Stirring (250 rpm); Stirring time (3 h)

Conclusion

This study was devoted for the elimination of basic dyes Au-O by adsorption on activated globe artichoke leaves. The equilibrium kinetics of adsorption of Au-O on GAL was reached after 30 min from time contact. The adsorption of auramine-O on activated globe artichoke leaves is described by Langmuir model satisfactorily with higher values of correlation coefficient R^2 of 0.8518. Kinetics studies also showed that the adsorption of the dye followed second-order kinetics ($R^2 = 0.999$). The results obtained in this work, have shown that GAL has an important power for Au-O removal since the ultimate adsorption capacity is 344.8 mg/g and it's shown that globe artichoke leaves is a promising adsorbent for the removal of auramine-O from aqueous solutions.

REFERENCES

1. K.R. Ramakrishna and T. Viraraghavan, *Water Sci. Technol.*, **36**, 189 (1997); https://doi.org/10.1016/S0273-1223(97)00387-9.
2. C.K. Lee, K.S. Low and P.Y. Gan, *Environ. Technol.*, **20**, 99 (1999); https://doi.org/10.1080/09593332008616798.
3. A.S. Özcan and A. Özcan, *J. Colloid Interface Sci.*, **276**, 39 (2004); https://doi.org/10.1016/j.jcis.2004.03.043.
4. J.J.M. Órfão, A.I.M. Silva, J.C.V. Pereira, S.A. Barata, I.M. Fonseca, P.C.C. Faria and M.F.R. Pereira, *J. Colloid Interface Sci.*, **296**, 480 (2006); https://doi.org/10.1016/j.jcis.2005.09.063.
5. Z. Aksu and S. Tezer, *Process Biochem.*, **36**, 431 (2000); https://doi.org/10.1016/S0032-9592(00)00233-8.
6. R.Y.L. Yeh and A. Thomas, *J. Chem. Technol. Biotechnol.*, **63**, 55 (1995); https://doi.org/10.1002/jctb.280630108.
7. V.M. Correia, T. Stephenson and S.J. Judd, *Environ. Technol.*, **15**, 917 (1994); https://doi.org/10.1080/09593339409385500.
8. M. Otero, F. Rozada, L.F. Calvo, A.I. Garcia and A. Moran, *Biochem. Eng. J.*, **15**, 59 (2003); https://doi.org/10.1016/S1369-703X(02)00177-8.
9. D. Suteu and D. Bilba, *Acta Chim. Slov.*, **52**, 73 (2005).
10. Y. Bulut and H. Aydin, *Desalination*, **194**, 259 (2006); https://doi.org/10.1016/j.desal.2005.10.032.
11. S. Chen, J. Zhang, C. Zhang, Q. Yue, Y. Li and C. Li, *Desalination*, **252**, 149 (2010); https://doi.org/10.1016/j.desal.2009.10.010.
12. M. Rafatullah, O. Sulaiman, R. Hashim and A. Ahmad, *J. Hazard. Mater.*, **177**, 70 (2010); https://doi.org/10.1016/j.jhazmat.2009.12.047.
13. E. Haque, J.W. Jun and S.H. Jhung, *J. Hazard. Mater.*, **185**, 507 (2011); https://doi.org/10.1016/j.jhazmat.2010.09.035.
14. M.S. El-Geundi, *Water Res.*, **25**, 271 (1991); https://doi.org/10.1016/0043-1354(91)90006-C.
15. K.C. Lakshmi, R. Narayan and A.K. Krishnaiah, *Indian J. Chem. Technol.*, **1**, 13 (1994).
16. H. Benaissa, *Scientific Stud. Res.*, **9**, 169 (2008).
17. K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani and S. Pattabhi, *Bioresour. Technol.*, **87**, 129 (2003); https://doi.org/10.1016/S0960-8524(02)00201-8.
18. G.O. El-Sayed, H.M. Aly, S.H.M. Hussien, *Int. J. Res. Chem. Environ.*, **1**, 132 (2011).
19. A.A. Attia, B.S. Girgis and S.A. Khedr, *J. Chem. Technol. Biotechnol.*, **78**, 611 (2003); https://doi.org/10.1002/jctb.743.
20. F.C. Wu, R.L. Tseng and C.C. Hu, *Micropor. Mesopor. Mater.*, **80**, 95 (2005); https://doi.org/10.1016/j.micromeso.2004.12.005.
21. S.K. Theydan and M.J. Ahmed, *Powder Technol.*, **224**, 101 (2012); https://doi.org/10.1016/j.powtec.2012.02.037.
22. F. Banat, S. Al-Asheh and L. Makhadmeh, *Adsorpt. Sci. Technol.*, **21**, 597 (2003); https://doi.org/10.1260/026361703771953613.
23. R.M. Shrestha, A.P. Yadav, B.P. Pokharel and R.R. Pradhananga, *Res. J. Chem. Sci.*, **2**, 80 (2012).
24. C. Namasivayam and D. Sangeetha, *J. Hazard. Mater.*, **135**, 449 (2006); https://doi.org/10.1016/j.jhazmat.2005.11.066.
25. Y. Guo, S. Yang, W. Fu, J. Qi, R. Li, Z. Wang and H. Xu, *Dyes Pigments*, **56**, 219 (2003); https://doi.org/10.1016/S0143-7208(02)00160-2.
26. R. Jain, M. Mathur and S. Sikarwar, *J. Sci. Ind. Res. (India)*, **65**, 258 (2006).
27. M. Valix, W.H. Cheung and G. McKay, *Chemosphere*, **56**, 493 (2004); https://doi.org/10.1016/j.chemosphere.2004.04.004.
28. N. Kannan and M. Meenakshisundaram, *Water Air Soil Pollut.*, **138**, 289 (2002); https://doi.org/10.1023/A:1015551413378.
29. A. Gurses, C. Dogar, S. Karaca, M. Acikyildiz and R. Bayrak, *J. Hazard. Mater.*, **131**, 254 (2006); https://doi.org/10.1016/j.jhazmat.2005.09.014.
30. A. Moussa, C. Abdelhamid, K. Samia, A. Tounsia and T. Mohamed *J. Environ. Anal. Toxicol.*, **5**, 264 (2015); https://doi.org/10.4172/2161-0525.1000264.
31. Y. Diao, W.P. Walawender and L.T. Fan, *Bioresour. Technol.*, **81**, 45 (2002); https://doi.org/10.1016/S0960-8524(01)00100-6.
32. W.-L. Chou, C.-T. Wang, C.-P. Chang, M.-H. Chung and Y.-M. Kuo, *Fresenius Environ. Bull.*, **20**, 78 (2011).
33. F.E. Okieimen, C.O. Okieimen and R.A. Wuana, *J. Chem. Soc. Nigeria*, **32**, 126 (2007).
34. B.H. Hameed, *J. Hazard. Mater.*, **162**, 344 (2009); https://doi.org/10.1016/j.jhazmat.2008.05.045.
35. M.C. Paiva, I. Ammar, A. Campos, R. Cheikh and A. Cunha, *Compos. Sci. Technol.*, **67**, 1132 (2007); https://doi.org/10.1016/j.compscitech.2006.05.019.

36. H. Yang, R. Yan, H. Chen, D.H. Lee and C. Zheng, *Fuel*, **86**, 1781 (2007); https://doi.org/10.1016/j.fuel.2006.12.013.

37. N. Sgriccia, M.C. Hawley and M. Misra, *Composites Part A*, **39**, 1632 (2008); https://doi.org/10.1016/j.compositesa.2008.07.007.

38. M. Le Troedec, D. Sedan, C. Peyratout, J. Bonnet, A. Smith, R. Guinebretiere, V. Gloaguen and P. Krausz, *Composites Part A*, **39**, 514 (2008); https://doi.org/10.1016/j.compositesa.2007.12.001.

39. W. Liu, K. Mohanty, L.T. Drzal, P. Askel and M. Misra, *J. Mater. Sci.*, **39**, 1051 (2004); https://doi.org/10.1023/B:JMSC.0000012942.83614.75.

40. S. Senthilkumaar, P.R. Varadarajan, K. Porkodi and C.V. Subbhuraam, *J. Colloid Interface Sci.*, **284**, 78 (2005); https://doi.org/10.1016/j.jcis.2004.09.027.

41. S. Senthilkumaar, P. Kalaamani, K. Porkodi, P.R. Varadarajan and C.V. Subburaam, *Bioresour. Technol.*, **97**, 1618 (2006); https://doi.org/10.1016/j.biortech.2005.08.001.

42. S. Lagergren, *K. Svenska Vetenskapsakad Handl.*, **24**, 1 (1898).

43. Y.S. Ho and G. McKay, *Process Biochem*, **34**, 451 (1999); https://doi.org/10.1016/S0032-9592(98)00112-5.

44. Y.S. Ho, *J. Hazard. Mater.*, **136**, 681 (2006); https://doi.org/10.1016/S0032-9592(98)00112-5.

45. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918); https://doi.org/10.1021/ja02242a004.

46. G. Mckay, H.S. Blair and J.R. Gardner, *J. Appl. Polym. Sci.*, **29**, 1499 (1984); https://doi.org/10.1002/app.1984.070290504.

47. M. Kilpatrick, L.L. Baker Jr. and C.D. McKinney Jr., *J. Phys. Chem.*, **57**, 385 (1953); https://doi.org/10.1021/j150505a001.