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EQUILIBRIUM STUDY ON ADSORPTION PROCESSES OF 4-NITROPHENOL AND 2, 6-DINITROPHENOL ONTO GRANULAR ACTIVATED CARBON

MIHAELA-CLAUDIA TERTIŞ[a], FLORINA IONESCU[a], MARIA JITARU[a]

ABSTRACT. Adsorption of 4-nitrophenol and 2, 6-dinitrophenol onto granular activated carbon has been studied. Adsorption experiments were carried out in a batch system and were followed by UV-Visible spectroscopy over a period of 120 min. Adsorption isotherms were derived at 25^{o}C and the isotherm data were treated according to Langmuir, Freundlich and Tempkin isotherm equations. The fitting of experimental data was tested and the parameters of these equations were determined. Based on the correlation coefficients both Langmuir and Freundlich models are suitable for the study (the squares of correlation coefficients are all > 0.97). Based on the values of normalized percent deviation *P*, the Freundlich model is suitable for 4-NP and the Langmuir model is suitable 2,6-DNP adsorption onto granular activated carbon type NORIT GAC 1240W (value of *P* less than 5). The calculated adsorption capacity values (q_{max}) are: 277.77 mg g^{-1} for 4-NP, respective 41.15 mg g^{-1} for 2, 6-DNP.

Keywords: *adsorption, nitrophenols, isotherm, activated carbon*

INTRODUCTION

Among the environmentally concerned substances, nitrophenols represent one of the most common groups of highly toxic water pollutants. The monosubstituted 4-nitrophenol is found in wastewaters discharged from various industrial activities such as pulp and paper industries, textile mills, steel plants, oil refineries, etc. [1]. This compound is also associated with agricultural activities as an intermediate for the production of pesticides, herbicides and insecticides [2].

Phenol and some of its derivatives are considered priority pollutants with a permissible limit of 0.1 mg mL^{-1} in wastewater [3-6] and must be removed from industrial effluents before discharge into environment. Particular attention has been given to 4-nitrophenol which presents some undesired effects and has a permissible limit of 0.06 mg mL^{-1} [3, 6].

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[a] *Research Centre LAF-INT-ECOL, Faculty of Chemistry and Chemical Engineering, "Babes-Bolyai" University, 11 Arany Janos Street, 400028*

Attempts have been made to remove mononitrophenols from wastewater by a number of methods: oxidation with strong oxidizing agents as H_2O_2 [7], biodegradation [8], biosorption [9], photo catalytic degradation [10], etc.

Adsorption is an efficient, simple and inexpensive method for the removal of organic pollutants. As adsorbents, activated carbons, polymeric resins, silica, fly ash, zeolites were commonly used. Activated carbons are preferred adsorbents in industrial processes even they had poor mechanical properties and difficult regeneration processes [11].

Phenolic compounds in aqueous solutions can exist as phenolate ions, depending on the pH of the solution. Conversion of phenol and nitrophenol derivatives to phenolate anions is negligible in water solutions considering its small acidic dissociation constants [12, 13].

RESULTS AND DISCUSSION

The equilibrium nitrophenols solutions concentrations were determined by the aid of the calibration curves equations, obtained from spectrophotometric measurements (UV-Visible spectrophotometer UNICAM HELIOS and DR2800 HACH-LANGE).

The equilibrium adsorption capacities of the adsorbent were calculated using equation (1).

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

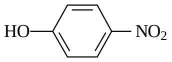
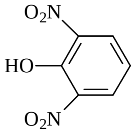
where q_e is the adsorption capacity of adsorbent material (mg nitrophenol/g of adsorbent); C_0 is the initial concentration of nitrophenol (mg L^{-1}); C_e is the equilibrium concentration of nitrophenol (mg L^{-1}); V is the volume of nitrophenol solution (L) and m is the mass of the adsorbent (g).

Adsorption characteristics and calibration data for nitrophenol derivatives

In water and acid solution, nitrophenols derivatives are in neutral form, with inessential amount of ionisation products [12, 13]. The spectral and calibration data for the studied compounds are given in Table 1.

It can be observed that both for 4-NP and 2, 6-DNP the UV-Visible spectra present two adsorption bands having significantly different values for the wavelength of maximum absorption (λ_{max}: 223 and 317nm in the case of 4-nitrophenol respective 222 and 430nm in the case of 2, 6-dinitrophenol). Although the calibration data were derived at both λ_{max} values for each compound, only one of them was utilized in this experiment due to the higher intensities of adsorption bands (ε = 9330 at 317nm for 4-NP respectively ε = 6280 at 430nm for 2,6-DNP).

Table 1. Spectral and calibration data for treated nitrophenol derivatives in water

Nitro phenol	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	Equation for calibration curve*	Standard deviation for *A*(%)	Regression coefficient (R^2)
4-NP 	317	9330	$C_{4-NP} = \frac{A}{0.2793}$	± 0.3÷1.4	$R^2 = 0.9902$
2,6-DNP 	430	6280	$C_{2,6-DNP} = \frac{A}{0.0194}$	± 0.4÷13	$R^2 = 0.9989$

* 7 calibration points for 4-NP; 14 calibration points for 2, 6-DNP; 3 different determinations for each calibration point.

The use of the data corresponding to the other two wavelengths of maximum adsorption, which have smaller values for ε, will affect the quantitative determination. On the other hand, due to the difference of about 100 nm between λ_{max} the method can be used for determination of both nitro phenols derivatives in water.

Adsorption isotherms

Adsorption isotherms at 25°C, derived for 4-nitrophenol and 2, 6-dinitrophenol in water, are shown in Figures 1(a) and 1(b). All the measurements were three times repeated and the values used represent the arithmetical mean of the correspondent three values.

The isotherm data were analyzed according to three well known isotherm equations: Langmuir, Freundlich and Tempkin, whose liniarized forms are given in equations (2)-(4) respectively [14-16].

- The liniarized form for Langmuir isotherm equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \tag{2}$$

- The liniarized form for Freundlich isotherm equation:

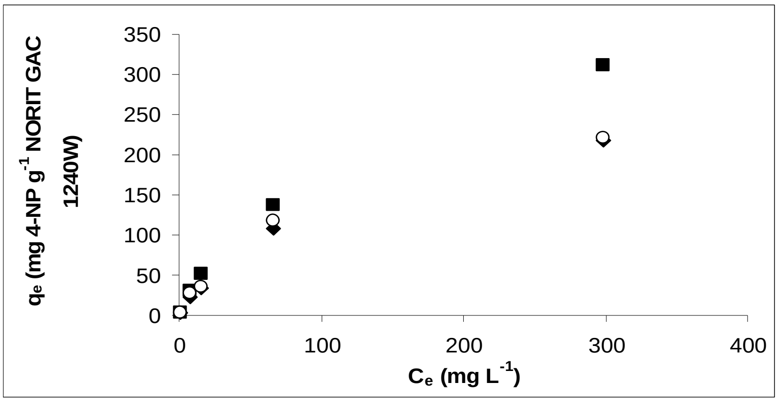
$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e \tag{3}$$

- The liniarized form for F Tempkin isotherm equation:

$$q_e = k_1 \ln k_2 + k_1 \ln C_e \tag{4}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg nitrophenol g^{-1} NORIT GAC 1240W); C_e is the final concentration at equilibrium (mg L^{-1}); q_{max} is the maximum adsorption at monolayer coverage of surface (mg nitrophenol g^{-1} NORIT GAC 1240W); b is the adsorption equilibrium constant related to the energy of adsorption (L mg^{-1}); K_F is a Freundlich constant representing the adsorption capacity (mg g^{-1})(L mg^{-1})$^{1/n}$; n is a constant depicting the adsorption intensity; k_1 the Tempkin isotherm energy constant (L mg^{-1}) and k_2 the Tempkin isotherm constant. The main difference between these three isotherm models is in the variation of heat of adsorption with the surface coverage. Langmuir model assumes uniformity, Freundlich model assumes logarithmic decrease and Tempkin model assumes linear decrease in heat of adsorption with surface coverage.

(a)



(b)

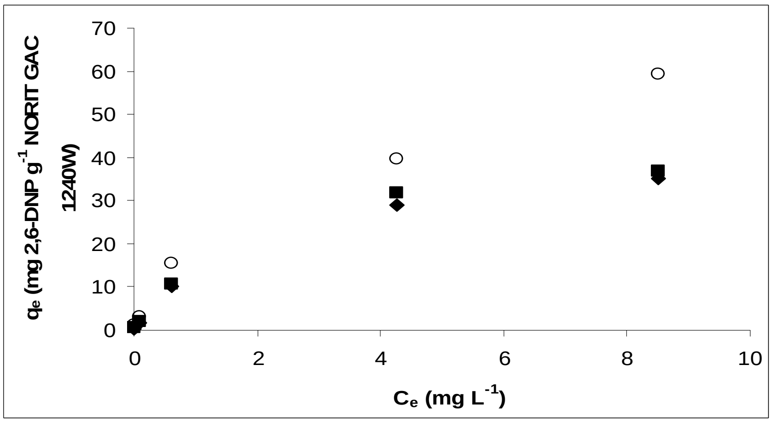
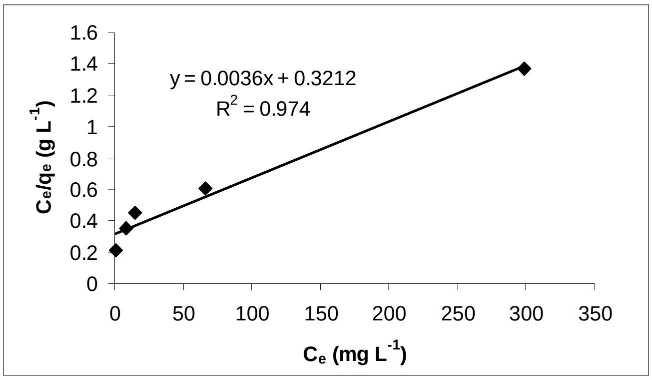


Figure 1. The fit of experimental data (♦) to Langmuir (■) and Freundlich (○) models at 25^{0}C for: (a) 4-nitrophenol and (b) 2, 6-dinitrophenol in water.

The Langmuir equation is valid for monolayer adsorption of adsorbate onto adsorbent surface and assumes there are a definite and energetically equivalent number of adsorption sites. The bonding to adsorption sites can either be chemical or physical, but it must be sufficiently strong to prevent displacement of adsorbed molecules along the surface. This model also presumes that molecules adsorbed on neighbouring sites do not interact each other [11, 17].

(a)



(b)

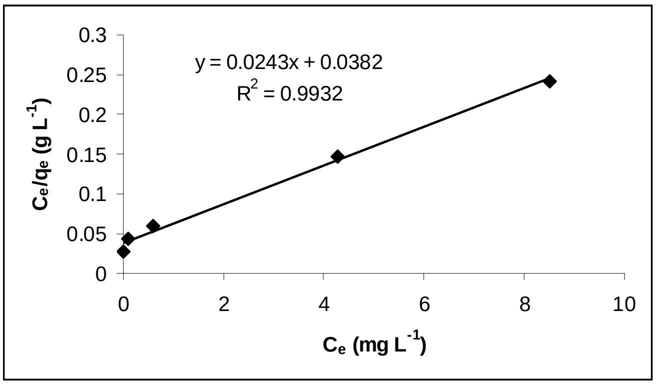


Figure 2. Linear form of Langmuir adsorption isotherm for: (a) 4-NP and (b) 2, 6-DNP adsorption on granular activated carbon type NORIT GAC1240W, at 25^{0}C.

The liniarized forms of Langmuir, Freundlich and Tempkin isotherm equations are given in equations (2)-(4), which describe these models. Figures 2-4 present the obtained results, and the parameters of these equations are given in Table 2.

Table 2. The equations parameters of Langmuir, Freundlich and Tempkin adsorption isotherm for nitrophenolic compounds at 25°C.

Nitro phenol	Langmuir parameters		Freundlich parameters		Tempkin parameters	
	$q_{\max}$ (mg g^{-1})	b (L mg^{-1})	K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	1/n	k_1 (L mg^{-1})	k_2
4-NP	277.77	86.44	2.04	1.52	33.6	0.59
2,6-DNP	41.15	0.63	2.01	2.30	5.4	36.39

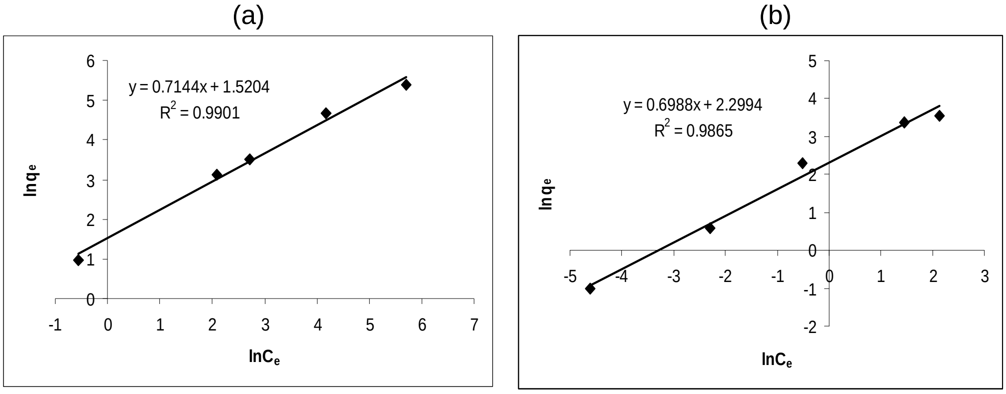


Figure 3. Linear form of Freundlich adsorption isotherm for: (a) 4-NP and (b) 2, 6-DNP adsorption on granular activated carbon type NORIT GAC1240W, at 25°C.

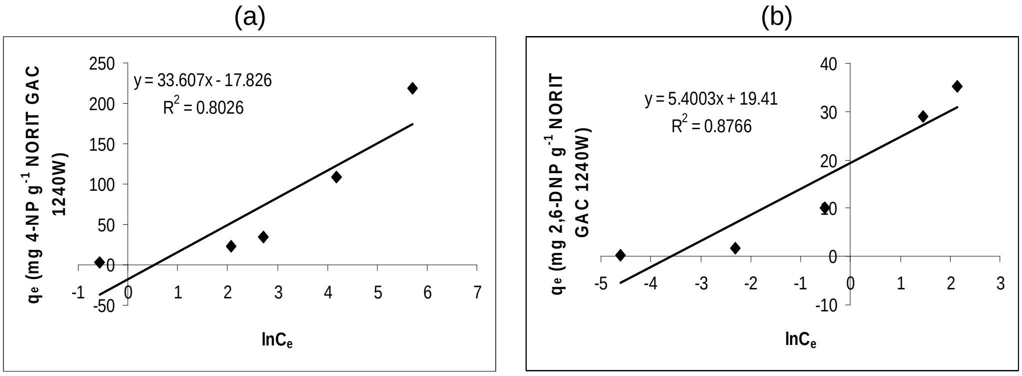


Figure 4. Linear form of Tempkin adsorption isotherm for: (a) 4-NP and (b) 2, 6-DNP adsorption on granular activated carbon type NORIT GAC1240W, at 25°C.

A better criterion to test the correlation between experimental data to one of the three isotherm equations (Langmuir, Freundlich and Tempkin), is a parameter known as normalized percent deviation [14], or percent relative deviation modulus, *P*, [15, 16], given by the equation (5):

$$P = \left(\frac{100}{N}\right)\Sigma\left(\frac{\left|q_{e(\exp)} - q_{e(pred)}\right|}{q_{e(\exp)}}\right) \tag{5}$$

where $q_{e(exp)}$ is the experimental q_e at any C_e; $q_{e(pred)}$ is corresponding predicted q_e according to the equation under study with best fitted parameters; *N* is the number of measurements (5 in our case). It is generally accepted that when the *P* value is less than 5, the fit is considered to be good [15]. The values for percent relative deviation modules, *P*, calculated for all three models and both nitrophenol derivatives are presented in Table 3. It can be seen that, in the case of 4-nitrophenol the value of *P* is less than 5 only for Freundlich model (*P*=0.9), and in the case of 2, 6-dinitrophenols for Langmuir model (*P*=2).

Table 3. Values of normalized percent deviations (P) for Langmuir, Freundlich and Tempkin models for nitrophenolic derivatives, at 25°C.

Nitro phenol	*P* Langmuir model	*P* Freundlich model	*P* Tempkin model
4-NP	10.99	0.90	26.60
2,6-DNP	2.00	26.20	80.00

The efficiency of adsorption process can be predicted by the dimensionless equilibrium parameter R_L, which is defined by the equation (6):

$$R_L = \frac{1}{1 + b \cdot C_0} \tag{6}$$

where *b* is the Langmuir constant (L mg^{-1}); C_0 the initial concentration of nitrophenolic compound (mg L^{-1}). Isotherm is considered to be unfavourable when $R_L > 1$, linear when $R_L = 1$, favourable when $0 < R_L < 1$ and irreversible when $R_L = 0$ [16, 18, 19].

The R_L calculated values are given in Table 4.

Table 4. Values of equilibrium parameter R_L for Langmuir, Freundlich and Tempkin models for nitrophenolic derivatives, at 25°C.

Nitro phenol	C_0 (mg L^{-1})	R_L
4-NP	13.91	0.46
	69.55	0.15
	139.11	0.08
	695.55	0.02
	1391.10	0.01
2,6-DNP	1.84	8.30×10^{-4}
	9.20	1.60×10^{-4}
	18.41	8.30×10^{-5}
	92.04	1.60×10^{-5}
	184.11	8.30×10^{-6}

Since all the R_L values calculated for treated nitrophenols are between 0 and 1, the adsorption processes are favorable in all cases.

CONCLUSIONS

In this study granular activated carbon type NORIT GAC1240W was used as adsorbent for 4-nitrophenol and 2, 6-dinitrophenol, to evaluate the applicability to remove these nitrophenols from water solutions. The experiments were conducted in a batch mode at constant working conditions. The equilibrium adsorption data were described by the Langmuir, Freundlich and Tempkin mathematical models. The values of the constants and correlation coefficients in all three models were calculated. Based on the correlation coefficients both Langmuir and Freundlich models are suitable for the study (the squares of correlation coefficients are all > 0.97).

According to the analysis of the results, and the values of normalized percent deviation *P*, the experimental data for 4-NP adsorption onto granular activated carbon type NORIT GAC1240W were correlated reasonably by the Freundlich model, unlike those for 2, 6-DNP adsorption which were correlated by the Langmuir model.

From the liniarized Langmuir equation, the calculated adsorption capacity values (q_{max}) are: 277.77 mg g^{-1} for 4-NP, respective 41.15 mg g^{-1} for 2, 6-DNP adsorption on granular activated carbon type NORIT GAC 1240W.

Because the equilibrium parameter R_L values are close to 0 ($10^{-5}\div10^{-6}$) for 2, 6-dinitrophenol at higher concentrations ($5\times10^{-4}\div10^{-3}$ mol L^{-1}), it is possible to presume that, in this condition, adsorption is irreversible. Future experiments are necessary to study the reversibility of the nitrophenol compounds adsorption onto activated carbon.

EXPERIMENTAL SECTION

Materials and methods

4-NP with purity greater than 98% (Merk, Germany), and 2, 6-DNP with purity greater than 95% (calculated based on dry substance), moistened with 20% H_2O (ALDRICH, Switzerland) were used to prepare the solutions, with desirable concentration, for the experiments in this study. Distilled water was used to prepare the aqueous solutions. All the reagents were analytical grade and used without further purification.

The activated carbon used in the present work was NORIT GAC 1240W, obtained from NORIT (Netherlands), having the following characteristics: micropores volume: 0.38 cm^3 g^{-1}; specific area: 1062 m^2 g^{-1}; mesopores volume: 0.45 cm^3 g^{-1}; apparent density: 495 kg m^{-3} [20].

Before use carbon was dried at 105^0C for 12 h and stored in desiccators at room temperature.

In adsorption experiments, the concentration of nonadsorbed 4-nitrophenol and/or 2, 6-dinitrophenol was determined from the absorbance of the species obtained spectrophotometrically at a wavelength of 316 nm for 4-nitrophenol and 430 nm for 2, 6-dinitrophenol. A Unicam Helios B spectrophotometer with the specific software VISION 32, and a quartz vat of 2 ml, with optical route of 1 cm, and a Direct Reading Spectrophotometer type DR/2800 HACH-LANGE with a quartz vat of 2 ml and with optical route of 1 cm were used to measure the adsorption intensities of the species.

The amount of the adsorbed nitrophenol was calculated from the equations which express the connection between the nitrophenols absorbance and concentration.

Batch adsorption experiments

Adsorption experiments were carried out using the conventional batch technique. Nitrophenol solutions were prepared by dissolving required amount of solid nitrophenol in distilled water. The initial concentrations of nitrophenolic compounds (between 13.91 and 1391.10 mg L^{-1} for 4-NP, respective 1.84 and 184.11 mg L^{-1} for 2, 6-DNP); the amount of activated carbon (1 g activated carbon to 0.2 L of nitrophenolic solution) and the temperature $(25\pm2)^0$C were kept constant during the adsorption experiments.

Isotherm tests

For adsorption isotherms tests, granular activated carbon was weighed and transferred to several glass containers. A known concentration of adsorbate solution was added and the containers were sealed and placed onto a TERMOMIX GRANT LTD6G thermostat where they were maintained at constant temperature of 25^oC for 48 h to ensure that equilibrium was reached. The adsorption experiments occurred under mechanical stirring (350 rpm) with an AGITUVAR 10W stirrer.

REFERENCES

1. Spectrum Laboratories, Chemical Fact Sheet – CAS # 100027; (http://www.speclab.com).
2. The International Programme on Chemical Safety (IPCS), Cincise, International Chemical Assessment Document 20 (CICAD), Mononitrophenols.
3. USEPA, Technical support document for water quality based toxics control, U.S. Environmental Protection Agency, Washington DC, USA, **1991**.
4. S.E. Manahan, "Fundamentals of Environmental Chemistry", CRC Press, Boca Raton, **2000**.
5. P.M. Alvarez, J.F. Garcia-Araya, F.J. Beltran, F.J. Masa, F. Medina, *Journal of Colloid and Interface Science*, **2005**, *283*, 503.
6. B. Pan, X. Chen, W. Zhang, X. Zhang, Q. Zhang, *Journal of Hazardous Materials*, **2006**, *137*, 1236.
7. Y.S. Li, Y.H. You, E.T. Lien, *Archives of Environmental Contamination and Toxicology*, **1999**, *4*, 427.
8. J-P. Arcangeli, E. Arvin, *Water Science and Technology*, **1995**, *31*, 117.
9. B. Koumanova, Z. Kircheva, *Journal of the University of Chemical Technology and Metallurgy (Sofia)*, **2003**, *38 (1),* 71.
10. M. Salaices, B. Serrano, H.I. de Lasa, *Chemical Engineering Science*, **2004**, *59*, 3.
11. M. Erdem, E. Yuksel, T. Tay, Y. Cimen, H. Turk, *Journal of Colloid Interface Science*, **2009**, *article in press,* doi: 10.1016/j.jcis.2009.01.014.
12. E. Ayranci, O. Duman, *Journal of Hazardous Materials B*, **2005**, *124*, 125.
13. J.B. Lambert, H.F. Shurvell, D. Lightner, R.G. Cooks, „Introduction to Organic Spectroscopy", Macmillan Publishers, New York, **1987**.
14. R-S. Juang, R-L. Tseng, F-C. Wu, S-H. Lee, *Separation Science and Technology*, **1991**, *26*, 661.
15. C.J. Lamauro, A.S. Bakshi, T.B. Labuza, *Lebensm-Wiss Technology*, **1985**, *18*, 111.
16. E. Ayranci, O. Duman, *Journal of Food Engineering*, **2005**, *70*, 83.
17. W.S. Wan Ngah, S. Fatinathan, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **2006**, *277*, 214.
18. K. Kadirvelu, C. Namasivayam, *Advances in Environmental Research*, **2003**, *7*, 471.
19. R. Sivaraj, C. Namasivayam, K. Kadirvelu, *Waste Management*, **2001**, *21*, 105.
20. I. M. Gullon, R. Font, *Water Research*, **2001**, *35*, 516.