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Adsorption of glyphosate onto activated carbon derived from waste newspaper

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ABSTRACT

This paper investigates the ability of activated carbon derived from waste newspaper (WNAC) to remove pesticide glyphosate from aqueous solution. The influence of initial pH was first studied. It was found that the WNAC presented the highest uptake capacity at pH 2.5. Adsorption isotherm models such as Langmuir, Freundlich and Redlich-Peterson were used to describe the adsorption of glyphosate by WNAC. The results show that the Langmuir adsorption isotherm model best fits the experimental data. The maximum adsorption capacity of WNAC is found to be 48.4 mg/g.

Keywords: Pesticide; Glyphosate; Adsorption; Waste newspaper activated carbon

1. Introduction

Pesticides are substance or mixture of substances which are generally used to prevent the destruction of agricultural crops by pest organisms including insects, plants, fungi, rodents and nematodes [1]. Glyphosate is a broad-spectrum, nonselective systemic herbicide used for control of plants including grasses, sedges, broad-leaved weeds, and woody plants. Glyphosate itself is an acid, but it is commonly used in salt form, most commonly the isopropylamine salt. Glyphosate has the following chemical structure [2]:

In Malaysia, demand for dlyphosate has increased substantially since the usage of herbicide Paraquat was banned in 2002 [3]. Extensive application of herbicides in agriculture has caused potential pollution in water sources and posed human health due to their toxicity and carcinogenicity. The EEC Directive for pesticides concentrations in water for human consumption with regard to potential health hazards is 0.1 mg/L [4].

The traditional water treatment, i.e. by chemical coagulation, clarification, rapid gravity filtration and slow sand filtration are effective only when the pesticides are very low water soluble [5]. The adsorption of pesticides on solid substrates such as soils, clays, microorganisms or activated carbon has been recognized as one of the effective techniques for the removal of pesticides from water. Adsorption onto activated carbon has received attention as the best available technology for the removal of many agrochemicals and other synthetic organic chemicals in drinking water [6]. The cost of commercial activated carbon is high due to the use of non-renewable and relatively expensive starting material such as coal. Consequently, low cost activated carbons are proposed for the removal of various pollutants. The cheap raw materials are usually provided from industrial and agricultural by-products [7]. Recently activated carbon produced from paper waste was reported [8].

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In this study, an attempt is made to prepare activated carbon by chemical activation of old newspaper. The produced activated carbon is evaluated for its ability to remove herbicide glyphosate from aqueous solution. The adaptability of different adsorption isotherm models to describe the experimental equilibrium data is also investigated.

2. Experimental

2.1. Preparation of chemically activated carbon

Activated carbon was produced using the procedure adapted from Okada et al. [9] and Méndez et al. [10]. Old newspaper was used to prepare activated carbon. Sample was first dried at 110°C before being impregnated in a KOH solution (4 water/4 sample/1 reagent, w/w ratio). After that it was dried again at 110°C for 2 h. Ten grams of samples were wrapped in aluminum foil and placed in a ceramic cup that was filled up with fuel coke particles. An electrical furnace (Vecstar Furnaces) was used and the temperature was increased to 650°C at a rate of 10°C min^{-1}. Final temperature was maintained for 2 h. As the temperature increases, O_2 in air was consumed by fuel coke particles and samples were pyrolyzed in the inert atmosphere generated. After activation, the samples were washed with distilled water to remove residual chemical reagent and the sample was dried at 110°C.

2.2. Characterization of the activated carbon

The size of activated carbon particles was measured by using mastersizer (HYDRO 2000 Mu, MALVERN). The apparent density of the material was obtained by weighting 5 g of the produced activated carbon and transferring it into a 10 mL graduated cylinder. Activated carbon was compressed in the cylinder and the volume was recorded. To calculate the apparent density, weight of sample was divided by recorded volume.

The specific surface areas (S_{BET}), pore volume and pore size distribution (PSD) of the samples were obtained from the N_2 adsorption–desorption isotherms measured using a constant-volume adsorption apparatus (Micromeritics Instrument, ASAP 2000).

The morphology of samples (carbonized and chemical activated carbon of paper wastes) coated with Au were observed by scanning electron microscope (SEM) at an accelerated voltage of 15 kV (S-3400N, Hitachi).

The pH of the point of zero charge (pH_{PZC}) was measured by the pH drift method. For this purpose, 50 cm^3 of a 0.01 M NaCl solution was placed in a titration vessel, thermostatted at 28°C. The pH was then adjusted to successive initial values between 2 and 12, by adding either HCl or NaOH and 0.15 g of WNAC was added to the solution. The final pH, reached after 48 h, was measured and plotted against the initial pH, as illustrated in Fig. 2. The pH at which the curve crosses the line $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$ is taken as the pH_{PZC} of the carbon, and is found to be 12.

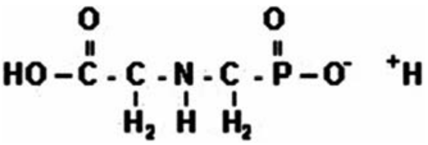


Fig. 1. The chemical structures of Glyphosate.

2.3. Materials

Analytical grade of herbicide glyphosate (N-(phosphonomethyl)glycine) was obtained from Crop Protection (M) Sdn. Bhd. All the reagents used were obtained from Sigma Aldrich and were of analytical reagent grade.

2.4. Measurement of glyphosate

Residual concentration of glyphosate was measured by using the method described in Glass [11] and Thabano et al. [12]. Glyphosate was oxidized to orthophosphate and the absorbance of phosphomolybdate heteropoly blue complex was measured by spectrophotometer (GENEYES 10 UV-USA) at 880 nm. Ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form a heteropoly acid (phosphomolybdic acid) that is reduced to intensely colored molybdenum blue by ascorbic acid. A reagent solution containing 50 mL 5N H_2SO_4, 0.01714 g potassium antimonyl tartrate, 0.6 g ammoniumolybdate and 0.528 g ascorbic acid were mixed. One drop of phenolphthalein indicator as well as 8.0 mL reagent were added to fifty milliliter samples with 5-20 mg/L of glyphosate. For higher concentration, the Glyphosate solution was diluted with distilled water to a concentration below 20 mg/L.

2.5. Effect of initial pH

The effect of pH on glyphosate adsorption onto WNAC was studied by adjusting the pH of glyphosate solutions with dilute HCl or NaOH solution in the range 2.0 to 9.0 and glyphosate concentration of 100 mg/L and WNAC dosage of 1 g/L.

2.6. Batch equilibrium study

To obtain the adsorption isotherm, 100 mL of glyphosate solution with initial concentration of 5, 10,

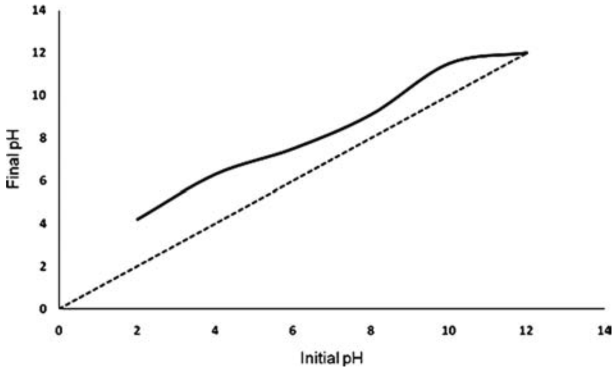


Fig. 2. pH drift method to obtain pHpzc.

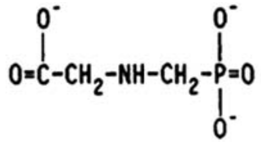
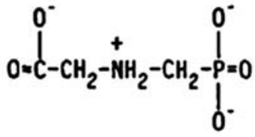
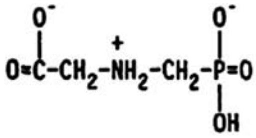
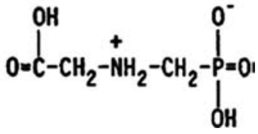
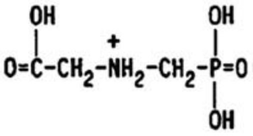
30, 40, 50, 60, 70 and 100 mg/L glyphosate was poured inside a 250 mL conical flask (Pyrex, England) which contained 0.1 g of activated carbon. To prevent evaporation, the conical flasks were covered with aluminum foil and then were shaken in an orbital incubator shaker, set at 150 rpm and 28°C (±2°C). The pH of the solutions was adjusted to 2.5. The glyphosate solutions were kept for 3 d to ensure equilibrium is achieved. To separate the adsorbent from the glyphosate solution, the sample was passed through filter paper and clarified solution was analyzed.

3. Results and discussion

3.1. *Effect of pH*

The pH of solution is one of the most important parameters affecting the adsorption process [13]. It can be observed from Fig. 2 that the adsorption of glyphosate changes with different initial pH. The maximum adsorption of glyphosate is at pH 2.5 and decreases significantly with further increase in pH. No adsorption of glyphosate is observed for pH greater than 8. It can be concluded that the adsorption is highly dependent on pH of the solution which affects the surface charge of the adsorbent, and the degree of ionization and speciation of the adsorbate. The carbon activated at high temperature consists of carboxyl, phenolic, alcoholic and quinone groups which results in negative charge surface that adsorbs H+ and exhibits a positive zeta potential [14,15]. The different species of dissociated glyphosate are listed in Table 1. It can be observed that glyphosate shows amphoteric characteristics with its phosphonate, carboxyl, and amine groups [16,17]. It can be observed that glyphosate is negatively charged at higher pH and it is expected that glyphosate removal increases with increasing pH. This contradictory result can be explained by the interaction of ionic and functional surface groups charge. The pHpzc is also used to explain the effect of pH. Fig. 3 shows the result of pHpzc obtained. When the pH of solution is below the pHpzc, the surface charge of the adsorbent is positive and it is negative when the pH is above the pHpzc [18]. When the pH value of the solution is below the pHpzc (pH < 12), the activated carbon surface becomes positively charged and exhibit an anion exchange capacity. Due to the fact that glyphosate is acidic, it exists as cations. Therefore, when the pH of solution is decreased the adsorption of glyphosate increases due to the positive surface charge of adsorbent. When the pH of solution is increased the density of positive charge sites decreases and the adsorption of glyphosate decreases due to repulsive force between adsorbent and adsorbate. The same observation was reported by Speth [17], and Namasivayam and Holl [19].

Table 1
Dissociation species for glyphosate

Range of pH	Dissociated Glyphosate
pH > 10.6	 $O{=}\overset{O^-}{C}{-}CH_2{-}NH{-}CH_2{-}\underset{O^-}{\overset{O^-}{P}}{=}O$
5.6 < pH < 10.6	 $O{=}\overset{O^-}{C}{-}CH_2{-}\overset{+}{NH_2}{-}CH_2{-}\underset{O^-}{\overset{O^-}{P}}{=}O$
2.6 < pH < 5.6	 $O{=}\overset{O^-}{C}{-}CH_2{-}\overset{+}{NH_2}{-}CH_2{-}\underset{OH}{\overset{O^-}{P}}{=}O$
2 < pH < 2.6	 $O{=}\overset{OH}{C}{-}CH_2{-}\overset{+}{NH_2}{-}CH_2{-}\underset{OH}{\overset{O^-}{P}}{=}O$
pH < 2	 $O{=}\overset{OH}{C}{-}CH_2{-}\overset{+}{NH_2}{-}CH_2{-}\underset{OH}{\overset{OH}{P}}{=}O$

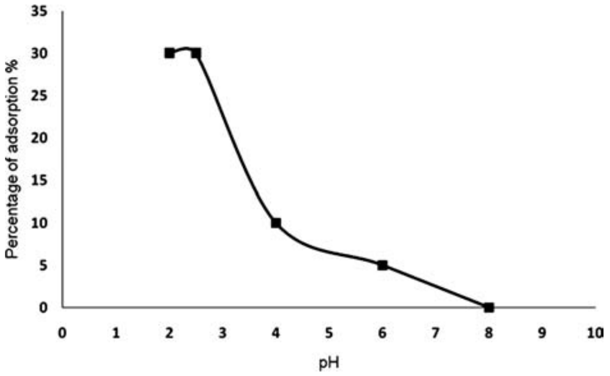


Fig. 3. Effect of pH on adsorption of Glyphosate onto WNAC.

3.2. Adsorption isotherm

Fig. 4 shows the SEM micrographs of newspaper waste. It can be observed that the carbonized newspaper waste has a smoother surface compared to the WNAC surface, suggesting that activation at 650°C with KOH resulted in the creation of more pores and a substantial removal of volatiles. The SEM-EDX analyses were simultaneously carried out for WNAC during the SEM examinations and the elemental analysis are given in Table 2. Table 3 presents the characteristics of waste newspaper activated carbon (WNAC). The WNAC produced in this work has a BET surface area of 535 m^2/g, which is lower than reported earlier in the literature. Shimada et al. [20] prepared activated carbon from old newspaper with phenol resin, by physical activation using steam. These activated carbons had specific surface areas of about 1,000 m^2/g. Okada et al. [9,21] prepared activated carbon from old paper by chemical activation and produced activated carbons having specific surface areas of about 1,700 m^2/g, which is even higher than commercial activated carbon. This suggests that there are still rooms to optimize the preparation conditions of our WNAC.

An adsorption isotherm describes the relationship between the amount of substance adsorbed by a unit weight of adsorbent and substance remaining in solution at equilibrium. Some isotherm models that could help to explain the solid–liquid adsorption of glyphosate on WNAC such as the Langmuir isotherm model (Eq. (1)), the Freundlich isotherm model (Eq. (2)) and the Redlich-Peterson isotherm model (Eq. (3)) were analyzed.

$$q_e = \frac{q_m \alpha_L c_e}{1 + \alpha_L c_e} \text{ or, alternatively } q_e = \frac{K_L c_e}{1 + \alpha_L c_e} \tag{1}$$

$$q_e = K_F C_e^{1/n} \tag{2}$$

$$q_e = \frac{K_R c_e}{1 + a_R c_e^{b_R}} \tag{3}$$

where q_e is solid phase concentration at equilibrium, C_e is solution phase concentration at equilibrium, α_L and K_L are Langmuir isotherm model constants, q_m is Langmuir monolayer saturation capacity, K_F and n are Freundlich isotherm model constants, K_R and α_R are Redlich-Peterson isotherm model constant and b_R is Redlich-Peterson isotherm model exponent.

Error analysis, sum of the square of errors (SSE) was performed to evaluate the divergence of each isotherm model from raw data, using Microsoft Excel Solver. The isotherm model constants are obtained using a non-linear regression by minimizing the SSE in order to avoid the change in error structure which is inherent bias resulting from linearization. The SSE is defined as:

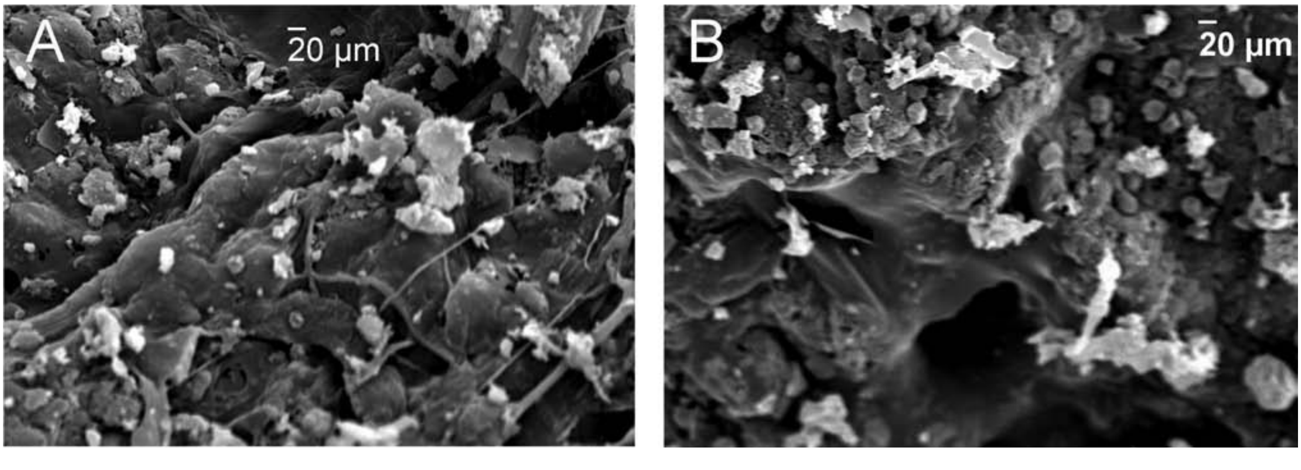


Fig. 4. SEM micrographs of newspaper wastes. (A) carbonized, (B) activated carbon from KOH at 650°C.

Table 2
SEM-EDX analyses (atomic percentage by element) of WNAC.

Element	C	N	O	Na	Al	Cl	Ca	Si
Weight %	13.25	7.8	67.4	0.075	3.78	0.19	2.84	4.9

$$\mathrm{SSE} = \sum (q_{\mathrm{e\,cal}} - q_{\mathrm{e\,exp}})^2, \quad (4)$$

where $q_{\mathrm{e\ exp}}$ and $q_{\mathrm{e\ calc}}$ are q_{e} from the experimental data and q_{e} from calculated data, respectively.

The glyphosate adsorption isotherms are shown in Fig. 5. The SSE analysis in Table 4 shows that all the three isotherm models describe the experimental adsorption data rather well. The SSE of the Freundlich and Redlich-Peterson isotherm models are very close. As shown in Fig. 4, these two isotherm models overlap each other. The lowest SSE is achieved using the Langmuir isotherm model. Based on Langmuir isotherm principles, the adsorption of adsorbate molecule takes places at identical sites and each site is for only one molecule. It is also assumed that energies of adsorption onto the surface of adsorbent are uniform with no transmigration of adsorbate in the plane of the surface, and the adsorbed molecules have no interaction [22,23]. It can be observed from Fig. 4 that the adsorption onto WNAC can be best described by using the Langmuir isotherm. The maximum adsorption capacity ($K_{\mathrm{L}}/\alpha_{\mathrm{L}}$) of WNAC obtained in this work is 48.4 mg/g. Bozkaya-Schrotter et al. [24] studied the removal efficiency or various pesticides using commercial activated carbon adsorption. The adsorption efficiency decreased with pesticide solubility. The adsorption capacity of glyphosate on WNAC prepared here is found to be comparable with commercial activated carbon.

4. Conclusion

The removal of glyphosate from aqueous solution by using activated carbon produced from old newspaper was investigated. The results of this study showed that waste newspaper can be successfully converted into activated carbon with BET surface area of 535 $\mathrm{m^2/g}$. It was found that adsorptions of glyphosate onto WNAC was fitted best using the Langmuir isotherm model with a maximum capacity of 48.4 mg/g. The maximum percentage of glyphosate removal was obatined at pH 2.5. The adsorption of glyphosate by WNAC decreased to zero when the pH is greater than 8.

Nomenclature

C_{e}	solution phase concentration at equilibrium
b	Redlich-Peterson isotherm exponent
D_{meso}	average mesopore diameter (Å)
K_{F}	Freundlich constant
K_{L}	Langmuir isotherm constant
n	Freundlich constant
q_e	Solid phase concentration at equilibrium
q_{e}	$_{\mathrm{xp}}$ q_{e} from the experimental data
q_{e}	$_{\mathrm{ealc}}$ q_{e} from calculated data
S_{BET}	BET specific syrface of activated carbon ($\mathrm{m^2/g}$)
V_{meso}	mesopore volume ($\mathrm{cm^3/g}$)

Table 3
Characteristics of waste newspaper activated carbon produced in this work.

Activated carbon	Average particle size (mm)	S_{BET} ($\mathrm{m^2/g}$)	V_{meso} ($\mathrm{cm^3/g}$)	V_{total} ($\mathrm{cm^3/g}$)	D_{meso} (Å)	Apparent density ($\mathrm{g/cm^3}$)
WNAC	< 0.1	535	0.123	0.3	23	0.67

Table 4
Isotherm model constants for Glyphosate sorption onto WNAC

Isotherm	Constants			SSE
Langmuir	α_{L} (L/mg)	$K_{\mathrm{L}}/\alpha_{\mathrm{L}}$ (mg/g)		
	0.025	48.4		4.8
Freundlich	K_{F} (mg/g)(L/g)$^{1/n}$	$1/n$		
	2.54	0.57		16.9
Redlich-Peterson	K_{R} (mg/g)(L/g)$^{1/\mathrm{b}}$	α_{R} (L/mg)^b	b	
	12.6	30.3	0.42	15.7

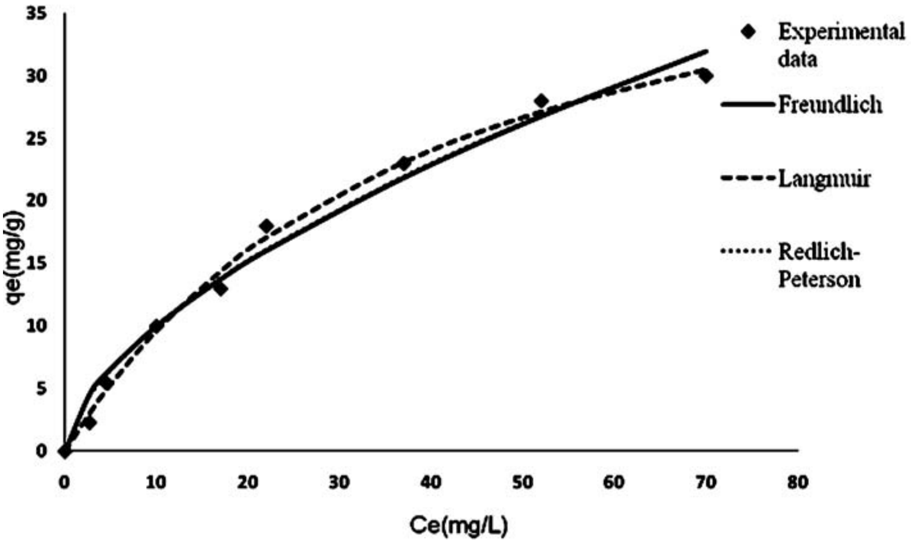


Fig. 5. Adsorption isotherms of Glyphosate onto WNAC.

V_{total}	total pore volume of acyivated carbon (cm^3/g)
α_L	Langmuir isotherm constant
α_R	Redlich-Peterson isotherm constant
ρ	density (g/cm^3)

Reference

[1] P.T. Holland, Pure Appl. Chem., 68 (1996) 1167–1193.

[2] A. Piccolo and G. Celano, Sci. Total Environ., 123 (1992) 77–82.

[3] W. Wibava, R. Mohamad, D. Omar and A. Juraimi, Weed Biol. Manage., 7 (2007) 242–247.

[4] V.K. Gupta, C.K. Jain, I. Ali, S. Chandra and S. Agarwal, Water Res., 36 (2002) 2483–2490.

[5] W. Inc, C. Inc, Industrial Waste Treatment Handbook, in Methods for Treating Wastewaters from Industry. Butterworth Heinemann, 2006, pp 149–334.

[6] Y. Matsui, D.U. Knappe and R. Takagi, Environ. Sci. Technol., 36 (2002) 3426–3431.

[7] B.H. Hameed, I.A.W. Tan and A.L. Ahmad, J. Hazard. Mater., 164 (2009) 1316–1324.

[8] N.R. Khalili, M. Campbell, G. Sandi and J. Golas, Carbon, 38 (2000) 1905–1915.

[9] K. Okada, N. Yamamoto, Y. Kameshima and A. Yasumori, J. Coll. Interf. Sci., 262 (2003) 179–193.

[10] A. Méndez, S. Barriga, J.M. Fidalgo and G. Gascó, J. Hazard. Mater., 165 (2009) 736–743.

[11] R.L. Glass, Anal. Chem., 53 (1981) 921–923.

[12] J.R.E. Thabano, C.T. Jens and G.M. Sawula, Talanta, 64 (2004) 60–68.

[13] S.Y. Cho, S.S. Park, S.J Kim and T.Y. Kim, Kor. J. Chem. Eng., 23 (2006) 638–644.

[14] J.L. Sotelo, G. Ovejero, J.A. Delgado and I. Martínez, Water Res., 36 (2002) 599–608.

[15] Z. Aksu and E. Kabasakal, Sep. Purif. Technol., 35 (2004) 223–240.

[16] J. Malik, G. Barry and G. Kishore, BioFactors, 2 (1989) 17–25.

[17] T.F. Speth, J. Environ. Eng., 119 (1993) 1139–1157.

[18] L.R. Radovic, I.F. Silva, J.I. Ume, J.A. Menéndez, C.A.L.Y. Leon and A.W. Scaroni, Carbon, 35 (1997) 1339–1348.

[19] C. Namasivayam and W.H. Holl, J. Chem. Technol. Biotechnol., 80 (2005) 164–168.

[20] M. Shimada, H. Hamabe, T. Iida, K. Kawarada and T. Okayama, J. Porous Mater., 6 (1999) 191–196.

[21] K. Okada, Y. Ono, Y. Kameshima, A. Nakajima and K.J.D. Mackenzie, J. Hazard. Mater., 141 (2007) 622–629.

[22] J. Limousin, J.P. Gaudet, L. Charlet, S. Szenknect, V. Barthès and M. Krimissa, Appl. Geochem., 22 (2007) 249-275.

[23] D.O. Cooney, Adsorption Design for Wastewater Treatment, Lewis Publishers, USA (1999).

[24] B. Bozkaya-Schrotter, C. Daines, A.S. Lescourret, A. Bignon, P. Breant and J.C. Schrotter, Water Sci. Technol., 8 (2008) 223–230.