Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.803650

52 (2014) 3510–3516
May

Taylor & Francis
Taylor & Francis Group

The removal of atrazine, simazine, and prometryn by granular activated carbon in aqueous solution

Cong Li[a], Li Wang[b], Yonggang Shen[a,*]

[a]*College of Civil Engineering and Architecture, Zhejiang University, Hangzhou 310027, China*
Fax: +86 571 87952015; email: sygdesign@zju.edu.cn
[b]*State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, China*

Received 13 December 2011; Accepted 23 April 2013

ABSTRACT

The removal of typical s-triazine herbicides including atrazine, simazine, and prometryn by granular activated carbon were studied under different temperatures (5, 10, 15, 25, and 35°C) and different water (distilled water, tap water, and river water). The results showed that the adsorptions of s-triazine herbicides in different. The adsorption of s-triazine is the greatest in distilled water and that is smallest in natural water. Moreover, for the adsorption isotherm, Freundlich model fitted the adsorption of s-triazine herbicides better than Langmuir model and the adsorptions of prometryn is the greatest, then that of atrazine and that of simazine is smallest.

Keywords: Granular activated carbon; S-triazine herbicides; Temperature; NOM

1. Introduction

The increase in production and use of pesticides for agriculture has resulted in the presence of a variety of persistent contaminants in the surface water and groundwater in recent years [1]. Although much benefit is obtained from their uses, they have some undesirable side effects such as toxicity, carcinogenity, and mutagenity [2–4]. The main compounds of this family, s-triazine, is found in many environmental compartments, contaminating soil and water. The s-triazines listed in the 76/464/EEC (black list) on pollution are atrazine (ATZ, 2-chloro-4-ethylamino-6-isopropylamino-1, 3,5-triazine), simazine (SIM, 1-chloro-3,5-bisethylamino-2,4,6-triazine), and prometryn (PRT, 2,4-bis (isopropylamino)-6-methylthio-1,3,5-triazine) [5]. These s-triazine herbicides are continuously accessing the environment due to their persistence in soils and hybrid sediments, caused by their low solubility in water [6]. As the wide use of these chemicals may pollute water resources and conventional water and wastewater treatment such as coagulation process and filtration process cannot effectively remove these herbicides, more effective removal methods for eliminating pesticides in water have been in urgent demand [7]. Some researchers studied the degradation of three typical s-triazine herbicides by ozone-based oxidation processes [8], also coupled with hydrogen peroxide [9], Mn(II) or UV radiation [10,11], and photocatalytic oxidation [12,13] in recent years. However, the results showed that complete s-triazine mineralization could not be attained due to the stability of the s-triazine ring.

For several decades, granular activated carbons (GAC) have been used in water treatment because of

*Corresponding author.

its known adsorbent properties [10–13]. Most of the adsorption of organic micropollutants on activated carbon during water treatment is influenced by a number of parameters such as concentration of micropollutants, pH, ionic strength, natural organic matters (NOM), and properties of activated carbon [14–17]. In this study, the temperature effects on adsorption of these s-triazine herbicides including ATZ, SIM, and PRT on GAC were investigated. Three s-triazine herbicides have similar basic chemical structures but with different substituent. They have different physicochemical properties, as shown in Table 1.

In addition, the removals of ATZ, SIM, and PRT by the GAC were compared under the different conditions including different initial concentration of s-triazine herbicides, different waters, and temperature.

2. Materials and methods

2.1. Chemicals

The s-triazine herbicides solutions were prepared by different waters including tap water from Shanghai city, distilled water and nature water from the Huangpu River. The basic characteristics of waters are given in Table 2.

ATZ, SIM, and PRT analytical grade (99.9% purity) were purchased from Aldrich. HPLC-grade solvents (acetonitrile and water) were supplied by Sigma Chemical Company (purity > 99%) [6].

Surface area and average pore diameter of GAC were measured using a specific surface analyzer (Micromeritics, ASAP-2020) at 77 K by nitrogen gas adsorption and a scanning electron microscope (SEM).

Table 1
The physicochemical properties of the herbicides studied

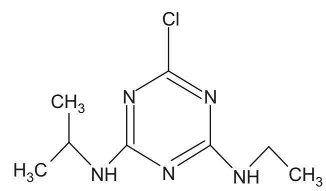
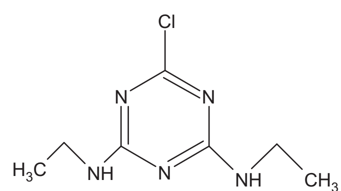
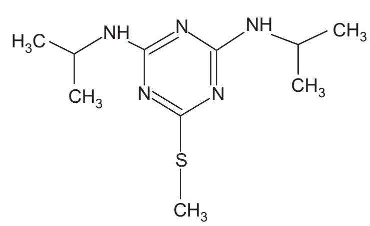
Chemical name	Molecular formula	Solubility (mg/L, 25℃)	Molar mass (g mol^{-1})	Chemical structure	Octanol/water partition coefficient K_{OW}
Atrazine (ATZ)	$C_8H_{14}ClN_5$	33	215.68		2.57
Simazine (SIM)	$C_7H_{12}ClN_5$	5	201.66		2.00
Prometryn (PRT)	$C_{10}H_{19}N_5S$	48	241.36		3.41

Table 2
Characteristics of different waters

Water	pH	DOC (mg/L)	Conductivity (μs/cm)	UV_{254} (cm^{-1})
Tap water	6.95–7.43	4.60–7.02	606–720	0.090–0.120
Distilled water	7.13–7.56	1.37–1.67	<20	<0.006
Natural water from the Huangpu River	6.9–7.5	7–10	792–950	0.120–0.210

The industrial GAC used in this study was from Tianjin Calgon Carbon Corporation. The iodine index and methylene blue index of GAC were 1,092 and 225 mg/g, respectively. Other chemicals used in this study were at least of analytical grade.

2.2. Experimental procedure

2.2.1. Adsorption behavior of s-triazine herbicides

The retained GAC samples were washed with deionic water and shaked for 10 min for three times to remove fine particles, then dried in a 105°C oven for 3 h to keep constant weight and cooled in a desiccators where it was stored prior to use. The equilibrium adsorption capacities of the GAC for ATZ, SIM, and PRT were determined by the bottle-point isotherm technique [18]. For adsorption studies, 0.1 g GAC and 200 mL of s-triazine solution with the initial concentration of ATZ (159–940 μg/L), SIM (152–949 μg/L), and PRT (154–890 μg/L) were introduced into 250 mL glass bottles and placed in a thermostatic bath shaker at the desired temperature 25 ± 0.5°C and 5 mL of aqueous sample was taken at each time interval.

2.2.2. Fractionation of natural organic matters

Prior to experiment, NOM was concentrated and fractionated into the nominal molecular weight (MW) fractions: <1,000, 1,000–3,000, 3,000–10,000, 10,000–30,000, >30,000 Da with ultrafiltration membranes (Dia. 90 mm) by prefiltering the nature water through a 0.45 μm Millipore filter (Dia. 50 mm).

2.3. Analytical methods

Three s-triazine herbicides including ATZ, SIM, and PRT were analyzed by a Shimadzu LC-2010 AHT HPLC (high performance liquid chromatography) equipped with a VP-ODS column (150 mm × 4.6 mm) and ultraviolet detector setting wavelength of 220 nm. Elution was performed with a mobile phase composed of acetonitrile/water at a flow rate of 0.8 ml/min. The dissolved organic carbon (DOC) concentrations were measured using a total organic compound (TOC) analyzer (TOC-VCPH, Shimadzu, Japan).

2.4. Mathematical model

Adsorption isotherms of s-triazine herbicides were calculated by means of the Freundlich equation [19] and Langmuir equation [20] as follows:

Freundlich equation:

$$q_e = \frac{x}{m} = k_f C_e^{1/n} \tag{1}$$

Langmuir equation:

$$\frac{q_e}{q_m} = \frac{k_L C_e}{1 + K_L C_e} \tag{2}$$

where q_e is GAC surface complex concentration at equilibrium in μg/mg, q_m is maximum adsorption capacity from Langmuir in μg/mg, k_f is the considered as a capacity parameter (and represents the uptake corresponding to a value of C_e equal to unit), k_L is Langmuir equilibrium constant (L/μg), C_e is the equilibrium concentration of adsorbate (s-triazine) in solution in μg/L, and n is a dimensionless parameter related to the site energy distribution.

3. Results and discussion

3.1. Characterization of granular activated carbons

According to the international Union of Pure and Applied Chemistry (IUPAC) classification, the pores may be subdivided in broad terms according to diameter (d) into a tortuous network of macropores ($d > 50$ nm), mesopores ($2 < d < 50$ nm), and micropores ($d < 2$ nm) [21]. In this study, physical properties of GAC are given in Table 3 and the scanning electron micrograph image of GAC is shown in Fig. 1.

As shown in Table 3 and Fig. 1, GAC in this study may be classified into mesopores carbon. The image presents for the amorphous carbon many pores. Moreover, FTIR spectrum of GAC is shown in Fig. 2.

As shown in Fig. 2, a broad peak between 3,100 and 4,000 cm^{-1} indicates the presence of both free and hydrogen bonded –OH groups on the absorbent surface. The bands appearing in spectra of GAC at 3,400 cm^{-1} indicate hydrogen bonding; and at 2,900 cm^{-1} is assigned to O–H stretching vibration originating in the molecule. It makes the adsorption of PRT with $–CH_3$ on GAC easier than SIM and ATZ with –Cl on GAC.

3.2. The adsorption of s-triazine herbicides

In order to make a comparative study for adsorption of three s-triazine herbicides, batch experiments

Table 3
Physical properties of granular activated carbons

Sample	BET surface area (m^2/g)	Average pore diameter (nm)	Micropore volume (cm^3/g)
GAC	950	2.80	0.23

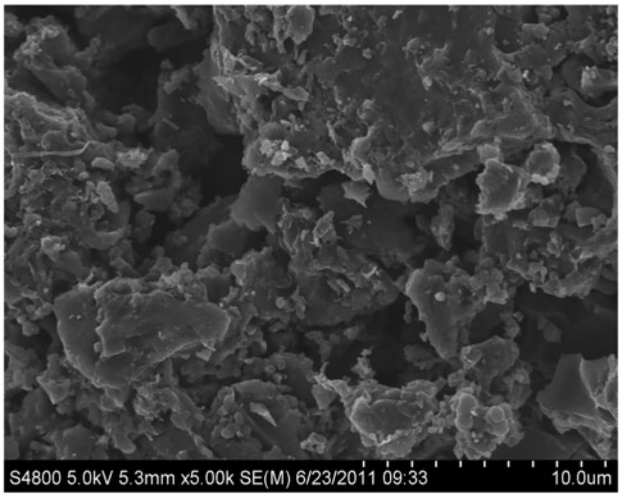


Fig. 1. Scanning electron micrographs of granular activated carbon.

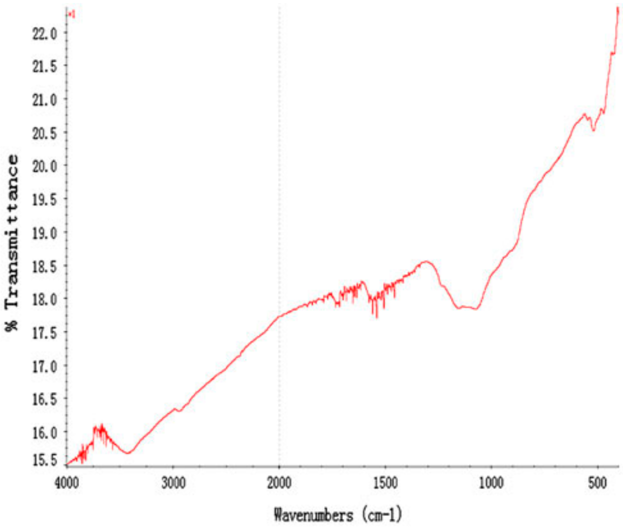


Fig. 2. FTIR spectrum of granular activated carbon.

were carried out with the initial concentrations of ATZ (159–940 μg/L), SIM (152–949 μg/L), and PRT (154–890 μg/L). The s-triazine solution was prepared by tap water. The Freundlich equation and Langmuir equation were used to fit the experimental data and the results were shown in Fig. 3.

It is seen from Fig. 3 that Freundlich model is more suitable than Langmuir model for three s-triazine adsorption. Langmuir equation which is called as the ideal localized monolayer model, because it is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between absorbed molecules. Freundlich equation assumes neither homogeneous

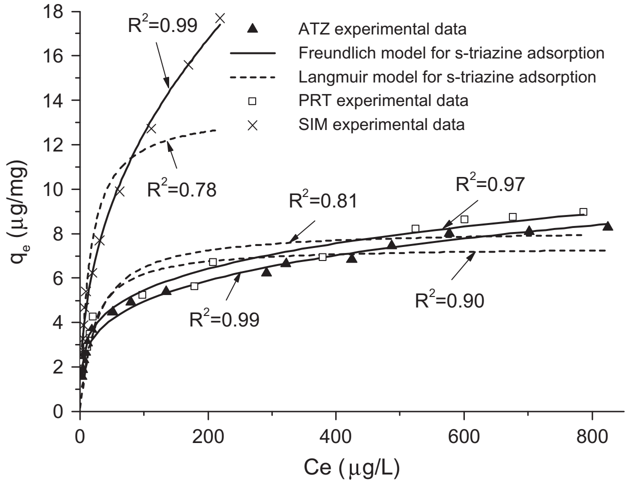


Fig. 3. Application of Freundlich and Langmuir models for s-triazine adsorption.

site energies nor limited levels of sorption and it is usually fits the experimental data over a wide range of concentrations. Therefore, Langmuir model, monolayer model, couldn't fit the experimental data well and Frendlich model fitted s-triazine adsorption better.

3.3. Adsorption behavior of ATZ herbicide at different temperatures

The effect of temperature on the adorption of s-triazine herbicides on GAC was studied. The adsorption of ATZ, SIM, and PRT at 15, 25, and 35°C was investigated. In the experiments, the s-triazine solution was prepared by tap water. The results were shown in Table 4.

It is seen from Table 4 that the adsorption decreases with temperatures increase. It confirms the exothermicity of s-triazine sorption process onto the

Table 4
Adsorption isotherm equation of three s-triazine herbicides on activated carbon under different temperatures

Temperature (°C)	Chemicals	Parameters of Freundlich model	R^2
15	ATZ	$q = 0.541C^{0.258}$	0.995
	PRT	$q = 1.322C^{0.235}$	0.991
	SIM	$q = 0.156C^{0.45}$	0.989
25	ATZ	$q = 0.459C^{0.273}$	0.982
	PRT	$q = 1.176C^{0.257}$	0.987
	SIM	$q = 0.118C^{0.48}$	0.980
35	ATZ	$q = 0.374C^{0.294}$	0.993
	PRT	$q = 0.996C^{0.281}$	0.990
	SIM	$q = 0.097C^{0.503}$	0.983

GAC. Moreover, as the DOC in tap water adsorption onto GAC enhances at higher temperature confirmed by results of Summers and Roberts [22], it make the adsorption of s-triazine decrease.

3.4. The adsorption of s-triazine in different waters

Several previous studies have shown that the presence of NOM could cause significant reduction in the GAC adsorptive uptake for target organic pollutants [23,24]. In this study, NOM was fractionated into five groups in terms of the nominal MW wanges: <1,000, 1,000–3,000, 3,000–10,000, 10,000–30,000, and >30,000 Da (filtered with 0.45 μm membrane). Fig. 4 shows MW distribution of NOM in different waters.

It is seen from Fig. 4 that MW above 3,000 Da of NOM in tap water is less than the NOM in nature water. Compare with nature water, MW of NOM is in the range of above 30,000, 10,000–30,000, 3,000–10,000 Da decrease 80.7, 57.5, and 38.7%, respectively. However, MW in the range of 1,000–3,000 Da and below 1,000 Da in tap water only decreases 4.0 and 1.6% and it nearly same with that of nature water. Therefore, main NOM of tap water and natural water was organics with MW below 3,000 Da. As the MW s of s-triazine follow the order: PRT > ATZ > SIM, Van der Waals force which is relative with MW and the adsorptions of prometryn is the greatest, then that of atrazine and that of simazine is smallest.

In order to investigate, the effect of NOM on the competitive s-triazine adsorption, s-triazine herbicide solutions were prepared with distilled water, tap water, and natural water from the Huangpu River. The adsorption isotherms of s-triazine herbicides were shown in Figs. 5(a–c).

It is seen from Figs. 5(a–c) that the adsorption of s-triazine is the greatest in distilled water and that is

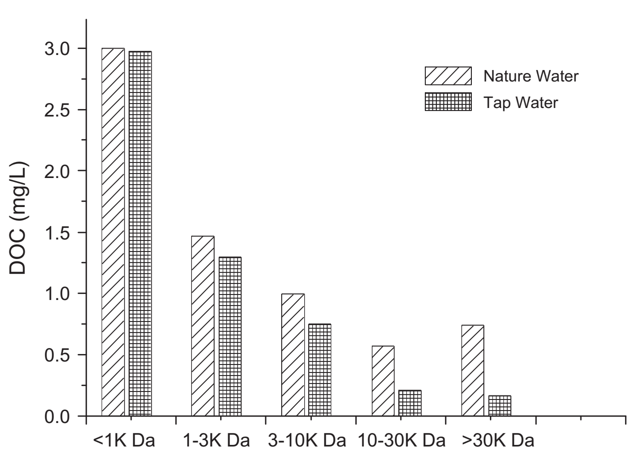


Fig. 4. MW distribution of NOM in different waters.

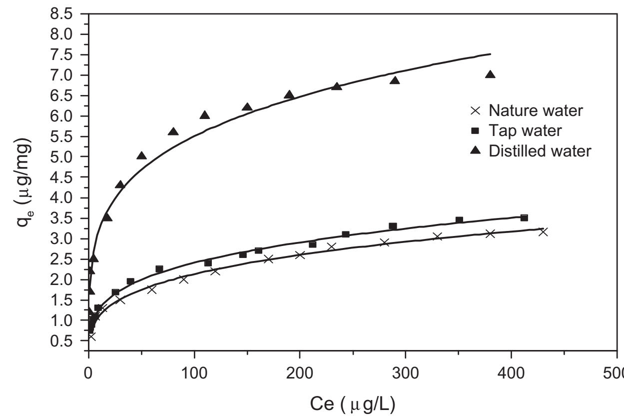


Fig. 5a. The adsorption isotherms of ATZ in different waters.

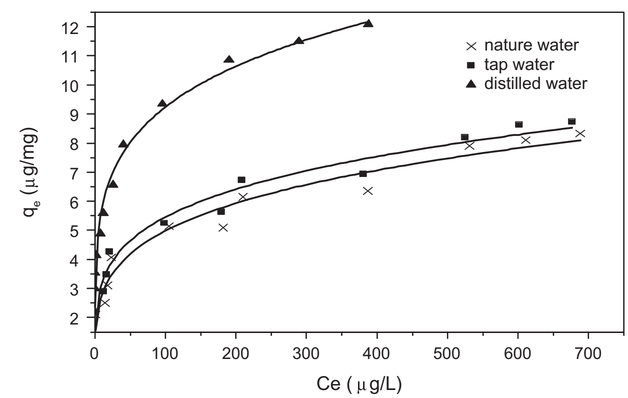


Fig. 5b. The adsorption isotherms of PRT in different waters.

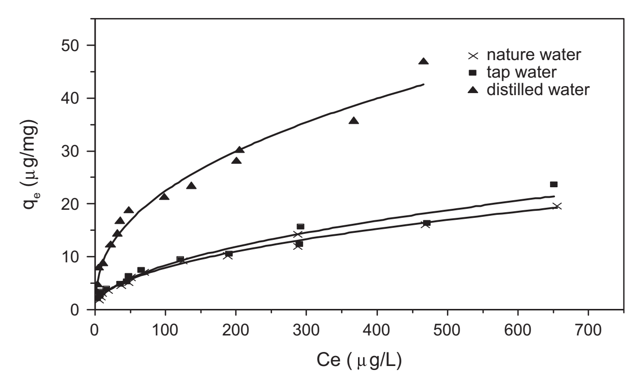


Fig. 5c. The adsorption isotherms of SIM in different waters.

smallest in natural water. The main reasons are that organics make competitive adsorption. Moreover, it is seen from Figs. 5(a–c) that the adsorptions of prometryn is the greatest, then that of atrazine and that of simazine is smallest. As the results of Fig. 4 show that

Table 5
Adsorption capacity comparison of three s-triazine herbicides on GAC in tap water

Chemicals	Parameters of Freundlich model	R^2
ATZ	$K_f = 1.3417$; $1/n = 0.2564$	0.972
PRT	$K_f = 1.8458$; $1/n = 0.2353$	0.986
SIM	$K_f = 0.8868$; $1/n = 0.4748$	0.990

MW of the main organics in tap water and natural water is below 3,000 Da, organics with small MW are competitive adsorption with s-triazine herbicide. The organics with MWs above 3,000 Da may plug the holes of GAC surface, and affect the adsorption of s-triazine on GAC. The adsorption parameters of s-triazine on GAC were compared with the similar initial concentration of s-triazine herbicides, shown in Table 5.

It is seen from Table 5 that K_f values of PRT, ATZ, and SIM are 1845.8, 1341.7, and 886.8 (μg/g) $(L/\mu g)^n$, respectively. $1/n$ values are 0.2353, 0.2564, and 0.4748, respectively. These results show the adsorption of prometryn is the greatest, then that of atrazine and that of simazine is smallest. As the adsorption of s-triazine herbicides on GAC was physical adsorption and the main force is Van der Waals force which is relative with MW. The MWs of PRT, ATZ, and SIM are 241.4, 215.5, and 201.5, respectively. Therefore, the adsorption of three herbicides decrease based on their MW, and which is consistent with Traube's Law.

4. Conclusions

This study demonstrated that the adsorption of s-triazine herbicides on GAC under different temperature, initial concentration of s-triazine herbicides, and different waters. The GAC adsorptions decrease with temperature increase. Moreover, the adsorption of s-triazine is the greatest in distilled water and that is smallest in natural water. The adsorption of prometryn is the greatest, then that of atrazine and that of simazine is smallest. In addition, the adsorption isotherms of these herbicides were fitted by Freundlich model and Langmuir model. Freundlich model fitted GAC adsorption of thee s-triazine herbicides better than Langmuir model.

Acknowledgments

This work was kindly supported by the foundation of key laboratory of Yangtze river water environment, ministry of education (Tongji University) (YRWEF201104), National Natural Science Foundation of China (Grant No. 51208455), Zhejiang Provincial Natural Science Foundation of China (Grant No. LY12E08017), and Research Fund for the Doctoral Program of Higher Education of China (Grant No. 20110101120033), the program for Zhejiang leading team of S&T innovation (2010R50037).

References

[1] G. Santacruz, E.R. Bandala, L.G. Torres, Chlorinated pesticides (2,4-D and DDT) biodegradation at high concentrations using immobilized *Pseudomonas fluorescens*, J. Environ. Sci. Health B 40 (2005) 571.
[2] C.S. Castro, M.C. Guerreiro, M. Goncalves, L.C.A. Oliveira, A.S. Anastácio, Activated carbon/iron oxide composites for the removal of atrazine from aqueous medium, J. Hazard. Mater. 164(2–3) (2009) 609.
[3] A. Kouras, A. Zouboulis, C. Samara, Th. Kouimtzis, Removal of pesticides from aqueous solution by combined physicochemical process—the behavior of lindane, Environ. Pollut. 103 (1998) 193.
[4] C. Li, N.Y. Gao, L. Wang, Photochemical degradation of typical herbicides simazine by UV/H_2O_2 in aqueous solution, Desalin. Water Treat. 36 (2011) 197.
[5] M. Fielding, D. Barcelo, A. Helneg, S. Galassi, L. Torstenson, P. van Zoonen, R. Wolter, G. Angeletti, Pesticides in ground and drinking water, Water Pollut. Res. Rep. Comm. Eur. Commun. Brussels 27 (1992) 1.
[6] C. Li, N.Y. Gao, Wang Li, T.Q. Zhang, Y.P. Zhang, S-triazine herbicides removal by granular activated carbon, Fresen. Environ. Bull. 21(6b) (2012) 1613.
[7] M.P. Ormad, N. Miguel, A. Claver, J.M. Matesanz, J.L. Ovelleiro, Pesticides removal in the process of drinking water production, Chemosphere 17(2) (2008) 225.
[8] J. Ma, N.J.D. Graham, Degradation of atrazine by manganese-catalysed ozonation – influence of radical scavengers, Water Res. 34(15) (2000) 3822.
[9] P. Huston, Degradation of selected pesticide active ingredients and commercial formulation in water by the photo-assisted Fenton reaction, Water Res. 33(5) (1999) 1238.
[10] N. Watanabe, S. Horikoshi, A. Kawasaki, H. Hidaka, N. Serpone, Formation of refractory ring-expanded triazine intermediates during the photocatalyzed mineralization of the endocrine disruptor amitrole and related triazole derivatives at UV-irradiated TiO_2/H_2O interfaces, Environ. Sci. Technol. 39(7) (2005) 2320.
[11] J. Rivas, E. Rodriguez, F.J. Beltran, J.F. Garcia-araya, P. Alvarez, Homogeneous catalyzed ozonation of simazine. Effect of Mn(II) and Fe(II), J. Environ. Sci. Health B 36(3) (2001) 317.
[12] D. Bamba, P. Atheba, D. Robert, A. Trokourey, B. Dongui, Photocatalytic degradation of the diuron pesticide, Environ. Chem. Lett. 6(3) (2007) 163.
[13] W. Chu, Modeling the quantum yields of herbicide 2,4-D decay in UV/H_2O_2 process, Chemosphere 44(5) (2001) 935.
[14] M. Yang, J. Hubble, A.D. Lockett, R.R. Rathbone, Thermal monitoring of phenoxy acid herbicide adsorption on granular activated carbon, Water Res. 31 (1997) 2356.
[15] E. Ayranci, N. Hoda, Studied on removal of metribuzin, bromacil, 2,4-D and atrazine from water by adsorption on high area carbon cloth, J. Hazard. Mater. B 112 (2004) 163.
[16] N. Daneshvar, S. Aber, A. Khani, A.R. Khataee, Study of imidaclopride removal from aqueous solution by adsorption onto granular activated carbon using an on-line spectrophotometric analysis system, J. Hazard. Mater. 144 (2007) 47.
[17] M.A. Javeed, S. Vigneswaran, W.G. Shim, J. Kandasamy, Removal of metsulfuron methyl by granular activated carbon adsorption, Desalin. Water. Treat. 21 (2010) 247.
[18] M.R. Graham, R.S. Summers, M.R. Simpson, B.W. Macleod, Modeling equilibrium adsorption of 2-methylisoborneol and geosmin in natural waters, Water Res. 34 (2000) 2291.

[19] M. Ulmer, A. Kräuter, H.J. Groβ, W.H. Höll, Adsorption aromatischer sulfonate an Aktivkohle: Untersuchungen zum Filterverhalten, GWF Wasser–Abwasser 141(5) (2000) 293.
[20] H. Humbert, H. Gallard, H. Suty, J.P. Croué, Natural organic matter (NOM) and pesticides removal using a combination of ion exchange resin and powdered activated carbon (PAC), Water Res. 42 (2008) 1635.
[21] K. Ohno, T. Minami, Y. Matsui, Y. Magara, Effects of chlorine on organophosphorus pesticides absorbed on activated carbon: Desorption and oxon formation, Water Res. 42 (2008) 1753.
[22] S.J. Randtke, V.L. Snoeyink, Evaluating GAC adsorptive capacity, J. Am. Water Works Assoc. 75 (1983) 406.
[23] H. Freundlich, Kapillarchemie, Akademische Verlagsgesellschaft, Leipzig, Germany, 1909.
[24] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361.
[25] M.W. Jung, K.H. Ahn, Y.H. Lee, K.P. Kim, J.S. Rhee, J.T. Park, K.J. Paeng, Adsorption characteristics of phenol and chlorophenols on granular activated carbons (GAC), Microchem. J. 70 (2001) 123.
[26] R.S. Summers, P.V. Robers, Activated carbon adsorption of humic substances: II. Size exclusion and electrostatic interactions, J. Colloid Interf. Sci. 122(2) (1988) 382.
[27] G. Newcombe, M. Drikas, R. Hayes, Influence of characterized natural organic material on activated carbon adsorption: II. Effect on pore volume distribution and adsorption on 2-methylisoborneol, Water Res. 31(5) (1997) 1065.
[28] Y.P. Zhang, J.L. Zhou, Removal of estrone and 17β-estradiol from water by adsorption, Water Res. 39(16) (2005) 3991.