Artigo de Revisão

POINT OF USE GRANULAR ACTIVATED CARBON FILTERS (POU) EFFICIENCY FOR ATRAZINE REMOVAL

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INFO ARTIGO

ABSTRACT

Atrazine is a concerning water sources contaminant that can remain at the drinking water. The objective of this study is to evaluate the efficiency of point of use (POU) filters with granular activated carbon to remove the contaminant, when added to deionized and natural well water under the theoretical concentrations of 1000.0 ng.L-1. The procedure used to quantify atrazine was the High-Performance Liquid Chromatography (HPLC), preceded by pre-concentration of the contaminants by solid phase extraction (SPE). Coconut carbon was evaluated, through preliminary tests carried out in "jar test" equipment, in order to obtain kinetic parameters, according to Freundlich equation. The parameters were inserted into a design model used in a complementary phase of the study, which evaluated the efficiency of filter prototypes in the removal of the contaminant in dynamic conditions. The results showed that the prototype filter, constructed from 90.0 g of coconut coal, which presented the highest efficiency for the removal of target pollutant in the preliminary trials, were able to reduce average 57.2% of atrazine after 1000.0 liters filtered, under predetermined operating conditions: flow rate 100 L.h-1 in continuous test. The filter prototypes were designed from the following Freundlich isotherms coefficients: q_{max} = 40.4 ng atrazine / mg carbon (maximum adsorption capacity); $1/n$ = 0.5138 and K_F = 1.10, with correlation coefficient of 0.9960.

1. Introduction

Household filters have aroused a growing interest in consumers from many countries lately. These devices, containing technology to improve the potable water quality from municipal sources, are usually composed of vegetable-based granular activated carbon (GAC) and enclosed in a plastic sump. Such devices are sized to fit into a certain flow rate range, considered adequate to several home applications and into a certain hydraulic pressure range, both established in the present local technical standards.

The population growth and concentration in Brazilian cities, the rising environment degradation, as well as the poor treatment of domestic and industrial wastewater, contaminating water sources, are the main reasons for people's lack of confidence about the water supplied to their homes. Additionally, the contamination of water sources by traces of chemical agents is important to highlight. These chemical agents are of anthropogenic nature and are present in the formulation of a variety of products and supplies available in the modern market. They are known as "emerging contaminants", many of them considered "endocrine disruptors", like atrazine, for instance; a substance largely employed in the agriculture as herbicide and frequently conveyed by the rain to the water sources, used later for the public supply through the municipal water treatment plants.

Atrazine quantification in potable water has been studied by many authors: Loos et al. (2007) verified its occurrence at concentrations between 3,0 and 16,0 ng/L; Verliefde et al. (2007) quantified 30 ng/L in Netherlands and Garcia-Ac et al., (2009) measured concentrations between 15 e 28 ng/L in potable water samples collected in Canada.

Other authors have reported atrazine in higher levels: Benotti et al., 2009 detected the contaminant at 990 ng/L in potable water in the US; Montagner (2011) detected it at a concentration from 8,3 up to 687 ng/L in

Brazil; Rinsky et al., (2012) reported it in the US at 8.900 ng/L.

On the other hand, authors like Yue (2006) reported the contaminant removal in deionized water, at a level of 97 and 84%, by means of carbon in fixed bed with mass values 77 and 136 grams, respectively, at a flow rate 2,4 L/h.

Atrazine has been chosen for this study for being a significant component in several agrochemicals, largely employed in crops like sugar cane, soybean, corn and coffee. Being agriculture one of the major pillars of the Brazilian economy, representing approximately 23% of the GDP in 2011, according to Delgado (2013), atrazine application and concentration should be proportional to the areas used for agriculture. The compound and its metabolites reach the water sources through surface runoff. In the potable water, it remains as traces, micro and nano grams per liter, due to the operations and processes used in conventional municipal water treatment plants being inefficient or not suitable. The Brazilian law establishes 2 µg/L as a maximum permitted concentration in the potable water for this substance.

2. Methods

The study was divided into two sequential steps: first step, static and second step, dynamic. The static step was carried out on a jar-test equipment, with the application of different amounts of granular activated carbon and two types of water: deionized and potable water, according to the Brazilian legislation (Portaria n° 2914/11 – Ministério da Saúde), both intentionally added to standard atrazine, at a concentration 1000 ng/L. The objective of the first step was to compare the adsorption process in both types of water and to adjust experimental data to Freundlich kinetic equation for potable water. They would be later on used to size the carbon beds of the filters evaluated in the dynamic step. Such tests represent the usual method to analyze water and wastewater treatment processes and to obtain many kinetic parameters related to the action of adsorptive agents when removing the contaminants. MOUSSAVI (2010); SURESH (2010); LIMA (2014); PRAMANIK (2015)

The dynamic step aimed the evaluation of atrazine removal from potable water with prototype filters, dynamically operated at a flow rate of 100 L/h. This step was started with the quantification of the granular activated carbon mass to be utilized in the prototypes considering the model proposed by Di Bernardo (2005). The model yielded an approximate mass of 30 grams for a complete removal of the contaminant at the flow rate used in this study. Considering this mass as a reference, prototypes were prepared with three different amounts of carbon: 30.0, 60.0 and 90.0 grams; corresponding to the value determined by the study, twice this value and three times, respectively. During the execution of this step, atrazine was quantified in filtered water samples collected in the beginning of the test and after a throughput of 8.0, 250.0, 500.0 and 1000.0. In attempt to be consistent with the previous step, room temperature was kept constant at 24.0±1.0°C by the HVAC equipment.

For atrazine quantification on the samples collected from the filter inlet and outlet, a pre-concentration technique was necessary, with a 2,000

times scale, by means of solid phase extraction with cartridges, since the contaminant concentrations were meager, (ng/L). The preparation of samples for the analyzes via HPLC (High Performance Liquid Chromatography) consisted of extraction with methanol, evaporation and elution with analyte. The extraction process was performed with extraction cartridges composed of the phase octadecyl silica (C18) with graphite carbon. Several scientific publications mention this technique like ATHANASIOS (2013); RENZ (2013); WANG (2013); LUO (2014); SNOW (2014); SELVARAJ (2014). HPLC is a consolidated analytical methodology for the quantification of emerging contaminants in water, including atrazine, and has been described by many authors like: NIEDERGALL (2014); JEWELL (2014); ALTMANN (2014); NAN (2014); CASAS (2015) e MONTAGNER (2007).

3. Results and discussion

The drinking water used in the tests had the following physicochemical characteristics: Turbidity: 0.118 ± 0.081 NTU; Apparent color: 1.0 CU, pH: 8.2 ± 0.1; Electrical conductivity: 199.6 ± 5.5 µS.cm-1; Organic matter: 14.5 ± 1.1 mg L-1; Total iron: 0.076 ± 0.020 mg L-1; Manganese: 0.013 ± 0.002 mg L-1; Total hardness: 74.0 ± 7.0 mg L-1; Total alkalinity: 92.5 ± 7.7 mg L-1 and TDS (total dissolved solids): 93.0 ± 3.0 mg L-1.

The GAC adopted at the study had the physical-chemical properties described at Table 1.

Table 1: physico-chemical properties – GAC

Properties	Carbon
Source	*Coco nucifera*
Brazilian region	Paraná (PR) - Brazil
Iodine index (mg I_2/g carbon)	Min 800
pH	6-8
Density (g/cm³)	0.40 – 0.55
Granulometry - passing in sieve 80 Mesh (%)	Max 5.0
Granulometry - retained in sieve 40 Mesh (%)	Max 5.0
Moisture (%)	Max 10

Static step:

Atrazine removal efficiency results for coconut carbon in deionized and potable water are shown at Table 2. The initial theoretical concentration was 1000,0 ng/L. The residual concentration presented correspond to an average from two values (i.e., 1 repetition) considering: jar-test equipment at constant room temperature, five types of carbon between 0 (blank) and 100.0mg, 1.0 (one) liter of water, constant stirring at 200 rpm (rotations per minute) and contact time 24 hours.

Table 2: Kinetic data obtained from atrazine reduction tests in deionized and well water, with free chlorine at 2.0 mg/L at an average temperature of 25.0±0.5°C, pH of 6.6 and contact time 24 hours

Deionized water with initial atrazine concentration of 1365.4 ng/L			Potable water with initial atrazine concentration of 1186.5 ng/L		
Atrazine average residual concentration (ng/L)	Granular activated carbon average mass (mg)	Average adsorptive capacity (ng atrazine/ mg of carbon)	Atrazine average residual concentration (ng/L)	Granular activated carbon average mass (mg)	Average adsorptive capacity (ng atrazine/ mg of carbon)
1141.1	3.1	72.4	1066.6	3.1	39.3
972.7	6.3	62.3	957.4	6.2	37.0
905.3	10.3	44.7	735.4	15.0	30.1
745.7	15.5	40.1	526.7	25.4	26.0
524.1	24.9	33.8	181.7	64.2	15.7
24.8	101.0	13.3			

Figure 1 shows Freundlich equation linearization graphs and Table 3 shows the parameters obtained from the model. Tests were performed with deionized and potable water with chlorine at 2.0mg/L

Atrazine in deionized water - Freundlich linearized model

$$y = 0,3904x + 0,5529$$
$$R^2 = 0,8978$$

Atrazine in potable water – Freundlich linearized model

$$y = 0,5138x + 0,0264$$
$$R^2 = 0,9918$$
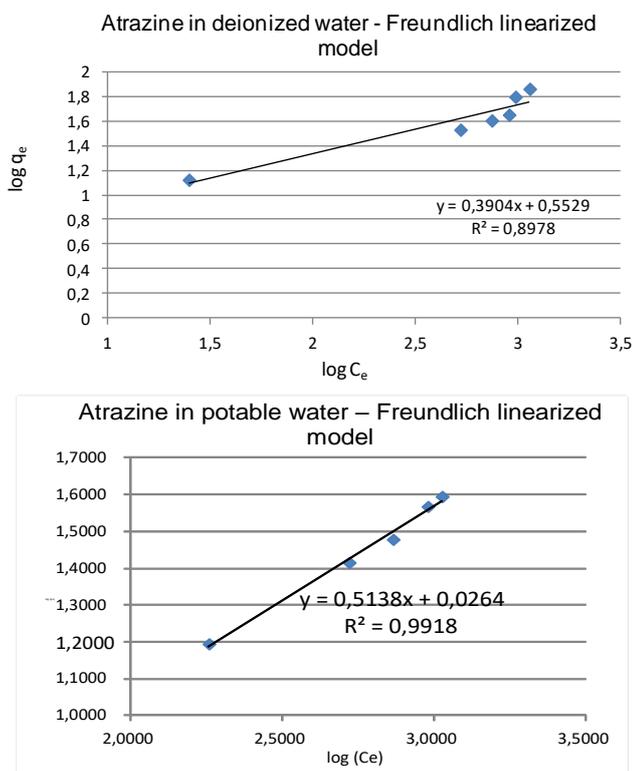
Figure 1: Graphs plotted from experimental data, adjusting the Freundlich equation to atrazine in deionized and potable waters with chlorine at 2.0mg/L, tested with coconut granular activated carbon.

Table 3: Kinetic constants experimentally determined by the application of Freundlich's model for atrazine in deionized and potable Waters with chlorine at 2.0mg/L, tested with coconut carbon

	FREUNDLICH MODEL - COCONUT CARBON				
Contaminant	Linearized equation	Equilibrium constant K (ng/mg).(L/ng)$^{1/n}$	1/n	r	qmax (ng/mg)
Deionized water	log qe = 0.3904.log Ce + 0.5529	3.57	0.3904	0.9475	61.8
Drinking water	log qe = 0.5138.log Ce + 0.0264	1.10	0.5138	0.9959	40.4

A comparative analysis of Freundlich equation parameters obtained for atrazine indicate an increase in the parameter "1/n" and decrease in the parameters "k" and q_{max}, when deionized water is replaced by potable water. The parameter "k" was reduced from 3.57 for deionized water to 1.10 (ng/mg)(L/ng)$^{1/n}$ for potable water. This can be directly associated to the presence of interferents, such as chlorine and its byproducts, natural organic matter, salts and metallic elements which, somehow, try to compete with atrazine for carbon active sites, in the adsorption process. A reduction in the parameter q_{max} was also observed for potable water compared to deionized water, from 61.8 to 40.4 ng of atrazine per mg of carbon.

Other authors have also reported the same reduction in the maximum atrazine adsorption capacity, when the adsorption studies migrate from deionized water to natural waters. Knappe (2009) observed a reduction in the maximum adsorption capacity for atrazine, when the test water was changed from deionized to natural, containing organic matter (water from River Sena – France). In one of his experiments the parameter "k" from the Freundlich equation changed from 2.46 to 0.898 (mg/g). (L/μg)$^{1/n}$, same behavior observed in this study. The author assigns the reduction in the adsorption capacity to the competitive coadsorption of the pores by compounds in the organic matter quantified in the water. Li (2003) studied the competition between atrazine and 1,4-dichlorobenzene in the presence of natural organic matter in attempt to evaluate its interference on atrazine adsorption levels, utilizing Freundlich Isotherm for different types of coconut granular activated carbon. A 74% adsorption capacity reduction was noted for atrazine and assigned to the competition of the compounds in the micropores. According to the author, if the isotherms obtained for water with organic matter are parallel to those plotted for distilled water, there is a small interference due to pore blocking by the organic matter in the adsorption process.

Pelekani e Snoeyink (2000) studied the removal of the pesticide Alaclor from water with hulmic acid by the application of granular activated carbon. There was a 31% decrease in the constant "k", when compared to the same test performed with distilled water. Ultimately, Coelho (2012) also associated the reduction in the Freundlich parameter "k" to the competition of organic matter and atrazine molecules for micropores. It changed from 104.71 to 74.13 [(mg.g-1).(L.mg-1)$^{1/n}$] when the test changed from distilled to natural water.

Dynamic step:

Table 4 shows GAC mass values calculated using experimental parameters obtained from Freundlich

equation for atrazine in natural well water, according to the model proposed by Di Bernardo (2005).

Table 4: Parameters calculated from Freundlich coefficients to determine the GAC mass value to be used in the prototypes

Freundlich model			
Contaminant:	**ATRAZINE**		
Freundlich parameters:	**q $_{máx}$**	**1/n**	**K**
Adsorbed mass for C$_e$ = C$_0$:	qe$_0$ (ng atrazine/ mg carbon)		
	36.33		
Volumetric rate:	TV (L of filtered water/ L of carbon)		
	19620.8		
Carbon usage rate:	TU (g of carbon / L of filtered water)		
	27.52		
Bed volume:	V $_{GAC}$ (cm^3)		
	0.0510		
Bed mass:	m $_{GAC}$ (g)		
Total bed mass (g):	27.52		

Figure 2 shows dynamic test results obtained by means of potable water quality monitoring from the prototypes. The concentration values correspond to that of the beginning, relative to the time zero (0% of filtrate volume), intermediate concentrations at the outlet, being collected at 1, 25, 50 and 75% of the total volume and the final concentration at 100% or 1000L. The values shown concern experiments carried out in triplicate.
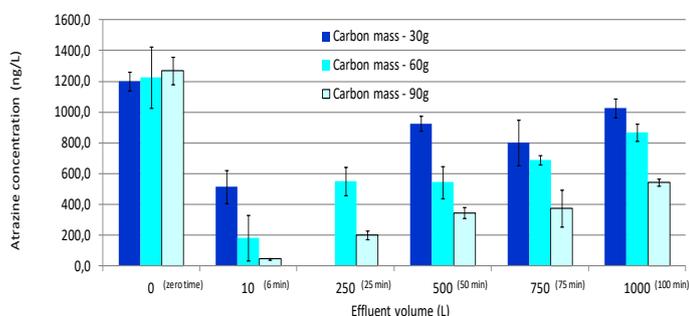
Figure 2: Experimental results regarding atrazine concentration (ng/L) at the prototype filters outlet. Prototypes built with 30.0, 60.0 and 90.0 grams of coconut granular carbon, operated at constant and continuous flow rate of 100 L/h, room temperature 25.0±1.0°C and pH 8.1, monitored at the beginning of the test and at 1, 25, 50, 75 and 100% of the total volume established for this study (1000L), corresponding to the filtration times 0, 6, 25, 50, 75 and 100 minutes, respectively

4. Conclusions

An atrazine reduction of 57.3 ± 21.0% was obtained for prototypes with 30.0 g of carbon after filtering 10L. That was the greatest average efficiency observed among all other monitored points, even considering the experimental error given by the standard deviation. After 1000L, the quantified removal efficiency was 14,4 ± 6,1%. For 60.0g prototypes, the highest removal efficiency was observed after 500L or 50% of the total tested volume (1000L). At this point, the efficiency value obtained for atrazine filtration was 55,6 ± 19,7%. However, if the standard deviation at each point is considered, the removal efficiency for volumes 250, 500 and 750L can overlap. After 1000L filtered, the average removal efficiency noted was 29.2±6.3%. Ultimately, for 90.0g prototypes, the percentage removal noted at the point corresponding to 10L of filtered water was 96.5±12.4%. In the subsequent water outlet samples, the removal values noted were 84.3 ± 14.3% ; 72.8 ± 10.2%; 70.4 ± 31.9% and 57.2 ± 4.0% after 1000L filtered.

The values of atrazine removal efficiency noted (percentage, relative to the initial concentration) at the three amounts of carbon in the prototypes can be considered consistent, since the incremental carbon mass caused an increasing atrazine concentration reduction at the filter outlet samples. Among the three alternatives studied, the most efficient for contaminant removal was that containing 90,0g of carbon for having shown superior to the other prototypes, in all monitored points.

The data herein show that the utilization of point of use household drinking water filters can represent a protection barrier for the municipal water users to the casual presence of the contaminant atrazine, considered an endocrine disruptor.

References

ALTMANN, J.; RUHL, A.S.; ZIETZSCHMANN, F.; JEKEL, M. Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment *Water Research*, v. 55, p. 185–193, 2014

ATHANASIOS S. STASINAKIS, A.; NIKOLAOS S. THOMAIDIS, N.S.; ARVANITI, O.S.; ASIMAKOPOULOS, A.G. Contribution of primary and secondary treatment on

the removal of benzothiazoles, benzotriazoles, endocrine disruptors, pharmaceuticals and perfluorinated compounds in a sewage treatment plant *Science of The Total Environment* v. 463–464, p. 1067–1075, 2013

BENOTTI, M.J., TRENHOLM, R.A., VAN DER FORD, B.J., HOLADY, J.C., STANFORD B.D., SNYDER, S.A. Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water; *Environmental Sciences and Technology.;* 43, p 597, 2009

BRASIL. Portaria nº 2914 de 12 de dezembro de 2011– Ministério da Saúde

CASAS, M.E.; BESTER, K. Can those organic micro-pollutants that are recalcitrant in activated sludge treatment be removed from wastewater by biofilm reactors (slow sand filters)? *Science of The Total Environment* v. 506–507, p. 315–322, 2015

COELHO, E.R.C.; VAZOLLER, H.; PEREIRA, W. Emprego do carvão ativado para remoção de atrazina em água de abastecimento público *Engenharia Sanitária e Ambiental*, v.17; n.4; p. 421-428, 2012

DELGADO, G. O **sentido da política econômica que dirige o Governo Dilma** Correio da Cidadania, 2013. http://www.correiocidadania.com.br. Access on 09/25/2013

DI BERNARDO, L.; Dantas, D. A. ; Métodos e técnicas de tratamento de água – Rio de Janeiro; ABES; 2005. 1565 ed. 2 vol. 2 Rio de Janeiro, R.J. RiMa

GARCIA-AC A., SEGURA P.A., VIGLINO L., FÜRTÖS A., GAGNON C., PRÉVOST M., Sauvé S. On-line solid-phase extraction of large-volume injections coupled to liquid Chromatography-tandem mass spectrometry for the quantitation and confirmation of 14 selected trace organic contaminants in drinking and surface water; *Journal of Chromatography A; v.* 1216; p. 8518, 2009

JEWELL, K.; TERNES, T.A. Comparisons between abiotic nitration and biotransformation reactions of phenolic micropollutants in activated sludge *Water Research* v. 48, p. 478–489, 2014

LI, Q.; SNOEYINK, V.L.; CAMPOS, C.; MARIÑAS, B.J. Elucidating competitive adsorption mechanisms of atrazina and NOM using model compounds. *Water Research*, v. 37, p. 773-784, 2003

LIMA, D.; BAÊTA, B.E.L.; AQUINO, S.F.; LIBÂNIO, M. Removal of Pharmaceuticals and Endocrine Disruptor Compounds from Natural Waters by Clarification Associated with Powdered Activated Carbon *Water, Air, & Soil Pollution,* 2014

MONTAGNER, C.C. *Ocorrência de interferentes endócrinos e produtos farmacêuticos nas águas superficiais da bacia do rio Atibaia* DISSERTAÇÃO DE MESTRADO Instituto de Química, Departamento de Química Analítica, Universidade Estadual de Campinas*,* 108p., 2007

MOUSSAVI, G.; KHOSRAVI, R. Removal of cyanide from wastewater by equilibrium analysis *Journal of Hazardous Materials* v. 183, n. 1–3, p. 724–730, 2010

LOOS, R., WOLLGAST, J., HUBER, T., HANKE, G. Polar herbicides, pharmaceutical products, perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and nonylphenol and its carboxylates and ethoxylates in surface and tap waters around Lake Maggiore in Northern Italy; *Anal. Bioanal. Chem.; n.* 387, p. 1469, 2007

LUO, X.; ZHANG, F. , JI, S.; YANG, B. Graphene nanoplatelets as a highly efficient solid-phase extraction sorbent for determination of phthalate esters in aqueous solution *Talanta* v. 120, p. 71-75, 2014

NAN, S. JO, B. Occurrence and removal of selected micropollutants in a water treatment plant *Chemosphere* v. 95, p. 156–165, 2014

NIEDERGALL, K.; BACH, M.; HIRTH, T. Removal of micropollutants from water by nanocomposite membrane adsorbers *Separation and Purification Technology* v. 131, 27, p. 60–68, 2014

PELEKANI, C. & SNOEYINK, V. Competitive adsorption between atrazine and metilene blue on activated carbon: the importance of pore size distribution. *Carbon*, v. 38, n. 10, p. 1423-1436, 2000

PRAMANIK, B.K.; RODDICK, F.A. A comparative study of biological activated carbon, granular activated carbon and coagulation feed pre-treatment for improving microfiltration performance in wastewater reclamation *Journal of Membrane Science* v. 475, p. 147–155, 2015

RENZ, L.; VOLZ, C., MICHANOWICZ, D.; FERRAR, K. A study of parabens and bisphenol A in surface water and fish brain tissue from the Greater Pittsburgh Area *Ecotoxicology* v. 22, n. 4, p. 632-641, 2013

RINSKY, J.L.; CLAUDIA HOPENHAYN, C.; GOLLA, V. Atrazine Exposure in Public Drinking Water and Preterm Birth *Public Health Reports* n. 127, v. 1, p. 72-80, 2012

SELVARAJ, K.K.; SHANMUGAM^A, G.; SAMPATH, S.; LARSSON, D.G.J.; RAMASWAMY, B.R. GC–MS determination of bisphenol A and alkylphenol ethoxylates in river water from India and their ecotoxicological risk assessment *Ecotoxicology and Environmental Safety* v. 99, p. 13-20, 2014

SNOW, D.; DAMON-POWELL, T.; ONANONG, S.; CASSADA, D. Sensitive and simplified analysis of natural and synthetic steroids in water and solids using on-line solid-phase extraction and microwave-assisted solvent extraction coupled to liquid chromatography tandem mass spectrometry atmospheric pressure photoionization *Analytical and Bioanalytical Chemistry* v. 405, n. 5, p. 1759-1771, 2014

SURESH, S.; SRIVASTAVA, V.C.; MISHRA, I.M. Isotherm, Thermodynamics, Desorption, and Disposal Study for the Adsorption of Catechol and Resorcinol onto Granular Activated Carbon J*ournal of Chemical & Engineering Data* v. 56, p.811-818, 2010

VERLIEFDE A., CORNELISSEN E., AMY G., BRUGGEN B.V., DIJK H. Priority organic micropollutants in water sources in Flanders and the Netherlands and assessment of removal possibilities with nanofiltration; *Environ. Pollut.*; v.146, p. 281, 2007

WANG, Z.; HAN, Q.; XIA, L.; DING, M. Graphene-based solid-phase extraction disk for fast separation and preconcentration of trace polycyclic aromatic hydrocarbons from environmental water samples *Journal of Separation Science* v. 36, n. 11, p. 1834–1842, 2013

YUE, Z.; ECONOMY, J.; RAJAGOPALAN, K.; PIWONE, M. Chemically activated carbon on a fiberglass substrate for removal of trace atrazine from water *Journal of materials chemistry* v.16, p. 3375-3380, 2006