Fluometuron Removal from Agricultural Wastewater in Porous Media Filters

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Fluometuron removal from agricultural wastewater in porous media filters

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Abstract

In the present study, six gravity filters were constructed and evaluated for the treatment of agricultural wastewater contaminated with herbicide fluometuron. Two filter types in terms of feeding strategy (i.e., batch and continuous feeding strategies), three porous media (i.e., coarse gravel, coarse zeolite and fine zeolite) and three hydraulic residence times (i.e., 1 day, 2 days and 4 days) were evaluated to find the best design and operation parameter in fluometuron removal by adsorption on porous media. Batch experiments were also conducted and the experimental data were fitted to adsorption kinetic and isotherm models. Results showed that the experimental data fitted better to the pseudo-first order model and to the Freundlich model, and the highest fluometuron adsorption was recorded for fine zeolite. The results of filter operation indicated that the most important parameter affecting fluometuron removal is the hydraulic residence time.

Keywords: Pesticides, Hydraulic residence time, Gravity filters, Adsorption kinetic models, Freundlich and Langmuir isotherms

1 Introduction

In modern agriculture, the use of pesticides and, in specific herbicides, insecticides and fungicides, is necessary to control weeds, insects and fungi, respectively, and can also lead to increased crop yields. However, if pesticides are not properly used and applied (that is, without complying to the principles of good agricultural practice), they can cause significant environmental risks. At the same time, they are considered responsible for global environmental pollution to a great degree (Konstantinou et al. 2006; Vryzas et al. 2009; Vallée et al. 2014). Runoff, leaching and groundwater drainage of agricultural fields are important forms of non-point source pollution, leading to degraded water quality in aquatic systems due to increased nutrient loads (Gikas et al. 2014, 2017) and pesticide entry (Vryzas et al. 2012; Papadakis et al. 2018). In addition, washing and filling of spray equipment, disposal of pesticide packages (empty containers), incorrect pesticide storage and accidents constitute other major forms of point source pollution (Vryzas et al. 2012; Reichenberger et al. 2007; Aktar et al. 2009).

Fate of pesticides depends on various factors such as soil properties, landscape characteristics, agricultural management practices, weather conditions especially heavy rainfall as well as physicochemical properties of pesticides (Schulz et al. 2001). The presence of pesticides in rivers, lakes, reservoirs and drainage networks has been documented in various studies around the world and, therefore, there is a risk for aquatic

53 organisms whose habitats are affected by them (Ccanccapa et al. 2016; Lefrancq et al.
54 2017). Environmental quality standards for certain substances, including many pesticides
55 characterized as priority pollutants, have been established for surface water by EU
56 (Directive 2008/105/EC 2008). Furthermore, the maximum admissible concentration for
57 potable water set by the EU (Directive 98/83/EC 1998) is 0.1 μg/L for individual
58 pesticides and 0.5 μg/L for the sum of pesticide concentration. Nevertheless, the
59 concentration of pesticide residues detected in surface- and ground-water bodies usually
60 exceeds the above thresholds.

61 Fluometuron, which is available in the market since the 1970s, is widely used as a
62 selective pre- and post-emergence herbicide to control annual grasses and broadleaf
63 weeds in cotton and other crops (PPDB 2016). High mobility and leaching of fluometuron
64 has been reported for soils with low organic matter content, as its sorption on soil is
65 influenced by organic matter content, whereas for permeable and sandy soils this may
66 result in ground water contamination (Cabrera et al. 2011). Fluometuron has been
67 detected in quite high concentrations in water bodies both in USA and Europe. In
68 particular, it has been detected in the Yazoo River Basin USA (Coupe et al. 2005) and in
69 the area of La Rioja Baja Spain (Herrero-Hernández et al. 2013) at concentrations of 6.42
70 μg/L and 18.36 μg/L, respectively. It has also been detected in three locations along the
71 Mississippi River as well as in its three tributaries at concentrations of 4-411 μg/L (Pereira
72 and Hostettler 1993). During the last decades, several pesticides were detected and
73 measured in surface and groundwater bodies in Greece. In the rivers and drainage canals
74 of Vistonis lagoon basin (North Greece) fluometuron was detected at high frequency
75 concentrations up to 317.6 μg/L, probably due to the fact that cotton is the main crop in
76 the area (Papadakis et al. 2015). Various pesticides, including fluometuron, which was

77 reported to have the highest concentration of 0.088 μg/L, were also detected in water
78 samples from Vistonis lagoon (Papadakis et al. 2015). Fluometuron was also found at
79 high frequency (25%) and at maximum concentration of 2.85 μg/L in the Strymonas river
80 basin, Northern Greece (Papadakis et al. 2018). Furthermore, Papadopoulou-Mourkidou
81 et al. (2004) reported the detection of several pesticides including fluometuron at
82 concentration of 1.95 μg/L in the Axios river, Northern Greece.

83 The results of the above studies indicate that the concentration of fluometuron in
84 surface water is often higher than the EU limit of 0.1 μg/L for drinking water (Directive
85 98/83/EC 1998). It is, therefore, necessary to reduce the amount of this herbicide ending
86 up in surface and ground waters. The most commonly used techniques to prevent and
87 mitigate pesticide entry into aquatic systems include: agricultural runoff treatment
88 through vegetated buffer zones (Prosser et al. 2020), constructed wetlands (CWs) and
89 planted ditches (Reichenberger et al. 2007). The removal of pesticides in CWs is
90 performed through natural (settling, adsorption), chemical (oxidation, reduction,
91 hydrolysis, photolysis, ion exchange) and biological processes such as plant uptake,
92 metabolism, microbial degradation (Imfeld et al. 2009; Papaevangelou et al. 2017; Gikas
93 et al. 2018a, b).

94 The effectiveness of CW systems in the removal of pollutants such as nutrients,
95 heavy metals and, organic compounds, is mainly related to their porous media, plant
96 species, wastewater residence time and climatic conditions (Papaevangelou et al. 2016,
97 Gikas et al. 2018a, b). The choice of the appropriate material as substrate in the CWs or
98 in gravity filters is important. Previous studies showed that zeolite filters, placed
99 downstream of vertical flow and horizontal subsurface flow CWs, increased pollutant

100 retention (e.g., phosphorus, ammonia nitrogen, etc.) and improved the effluent quality
101 (Stefanakis et al. 2009, 2012; Bruch et al. 2011).

102 There is, however, limited published literature on gravity filter applications in
103 agricultural wastewater treatment. Hence the aims of the present study were: (a) to
104 investigate the effectiveness of various porous media such as coarse gravel, coarse zeolite
105 and fine zeolite in removing by adsorption the herbicide fluometuron from contaminated
106 water that simulate agricultural runoff from point and non-point sources of pollution and
107 (b) to assess fluometuron adsorption capacity on various porous media using kinetic and
108 isotherm models.

109

110 ## 2 Materials and methods

111

112 ### 2.1 Physicochemical properties and characteristics of fluometuron

113

114 Fluometuron (CAS name: N,N-dimethyl-N′-(3-trifluoromethyl)phenyl)urea) is a
115 selective herbicide used for the control of annual broadleaf and grass weeds in cotton,
116 sugarcane and sesame (PPDB 2016). It acts systematically and is primarily absorbed by
117 the roots and secondarily by the foliage of plants thereby inhibiting photosynthesis. The
118 fate of the pesticides in the environment is a complex process and depends on their
119 physicochemical characteristics and properties such as water solubility, vapor pressure,
120 octanol-water partition coefficient (K_{ow}), sorption coefficient in the soil organic carbon
121 (K_{oc}), half-life in soil etc. (PPDB 2016). Table 1 shows the physicochemical properties
122 of fluometuron and, it can be seen that fluometuron has moderate solubility in water (111
123 mg/L at 20 ^{o}C), low bioaccumulation as the LogK_{ow} value is less than 2.7 and is non-

124 volatile as the Henry's law constant is less than 0.1 Pa m^3/mol (PPDB 2016). Depending
125 on the half-life for soil degradation, pesticides are divided into persistent, moderately
126 persistent and non-persistent with a half-life of more than 100 days, between 30 and 90
127 days and less than 30 days, respectively. Based on the above, fluometuron with a half-life
128 of 89.8 days for field studies is classified as moderately persistent.
129
130 **2.2 Filters configuration and operation**
131
132 The experiments of this study lasted from March 2017 to July 2017 and were carried out
133 at both the indoor and outdoor (in the open-air space) facilities of the Laboratory of
134 Ecological Engineering and Technology, Department of Environmental Engineering,
135 Democritus University of Thrace (location: 41° 08′ 47′′ N, 24° 55′ 09′′ E). In the open-
136 air space of the laboratory, six gravity filters were made: three for continuous and three
137 for batch (periodic) feeding. The filters were cylindrical plastic containers with a total
138 volume of 40 L. Each filter had an inlet at the top and an outlet which was controlled with
139 a valve. The outlet of the continuous feeding filters was connected to a vertical pipe which
140 ended to the upper level of the filter. Thus, the continuous feeding filters were always
141 operating in saturated conditions. At the bottom of each filter, a cobble layer of 5 cm was
142 first placed and then the porous media was placed at a thickness of about 30 cm (Figure
143 1). The filter and the pore water had volumes of 20 L and 7 L, respectively. Three porous
144 media were used: coarse-grained carbonate gravel (acronym: CG, D=8-16 mm), coarse-
145 grained zeolite (acronym: CZ, D=8-16 mm) and fine-grained zeolite (acronym FZ,
146 D=1.0-2.5 mm) so that each type of filter (continuous and batch feeding with acronym C
147 and B, respectively) would have three different fillers. Natural zeolite with the following

148 composition was used: clinoptilolite 88% (chemical formula $Ca_{1.7}K_1Mg_{0.6}Si_{29.8}O_{72}$
149 $20.4H_2O$), aluminum minerals 4%, silica 3% and others 5%.

150 In the present work, the removal of fluometuron by adsorption on the three porous
151 media was investigated for both feeding modes, batch and continuous loading, and for
152 hydraulic residence time (HRT) of one, two, and four days. Tap water enriched with
153 fluometuron at concentration of 40 mg/L was introduced into the filter units. In order to
154 prepare the influent of the filter units, the pesticide with trade name "Cottonex" with
155 fluometuron concentration 50% w/v was used. In batch feeding filters, the charge was
156 made once with 7 L of the above solution which remained in the filter for HRT of 1, 2 or
157 4 days. Then, the valve was opened and the whole solution (water enriched with
158 fluometuron) was released and the filter was refilled with 7 L of fresh solution. In the
159 continuous feeding filters, charging was carried out on a daily basis by adding an amount
160 of fluometuron solution equal to 7.0 L, 3.5 L and 1.75 L in order to achieve HRT of 1, 2
161 and 4 days, respectively. In these filters, the valve at the bottom of the containers was
162 always open and the level of the solution inside the containers was determined by the
163 height of the vertical pipe. The solution was added to the top of the filter while a
164 corresponding amount of solution overflowed from the vertical pipe. Throughout the
165 experiment, the containers (filters) were closed to prevent evaporation. Influent and
166 effluent water samples were collected on the day of loading regarding the batch feeding
167 filters and at a frequency of once every seven days regarding the continuous feeding filters
168 for instrumental analysis in the laboratory. Temperature (T), pH, dissolved oxygen (DO)
169 and electrical conductivity (EC) in the influent and effluent water of the six filter units
170 were measured *in situ* using WTW (Wissenschaftlich Technische Werkstätten, Germany)
171 series 197i portable instruments.

172

173 **2.3 Chemical analysis**

174

175 The water samples within 24 hours were extracted using solid-phase extraction (SPE)
176 technique. C18 (500 mg/6 mL) type cartridges fitted in a 12-fold vacuum manifold were
177 used for extraction following the method described by Vryzas et al. (2009). The cartridges
178 were activated by passing 5 mL of methanol (high purity, HPLC) followed by 5 mL of
179 ultrapure water at a rate of 1 mL/min. Then, 200 mL of water samples were passed
180 through the cartridges at a flow rate of 5 mL/min with the help of a vacuum. The cartridges
181 were then dried for 45 min followed by elution of the pesticides with 6 mL of mixture
182 methanol/ethyl acetate (1:9) at a flow rate of 1 mL/min. The eluates were evaporated
183 under a stream of nitrogen at 30 ^{o}C. The residue was redissolved in methanol and
184 subjected to the HPLC/PDA system for analysis (Vryzas et al. 2009). The system used
185 consists of a Thermo Scientific P2000 pump, a Thermo Separation Products 3000 sampler
186 and a Thermo Scientific 2000LP detector. Chromatographic separation was performed on
187 a 5 μm analytical HPLC column (Hypersil Gold 100x4.6). The mobile phase was a
188 gradient of methanol/water at a flow rate of 1 mL/min. The acquisition of the data was
189 performed at 215, 240 and 244 nm, quantification was conducted at 244 nm and the data
190 were processed using the Chrom Quest 5.0 software package. The analytical method was
191 validated at 3 fortification levels (0.1, 5, 10 mg/L). Recoveries ranged from 89 to 104 %
192 with RSD 7%. Moreover, the LOD and LOQ were 0.001 and 0.05 mg/L, respectively.

193

194 **2.4 Fluometuron adsorption experiments**

195

196 In order to assess the fluometuron adsorption potential on porous media, adsorption
197 kinetics and isotherm experiments were conducted. The selected porous media were
198 coarse-grained carbonate gravel (CG), coarse-grained zeolite (CZ) and fine-grained
199 zeolite (FZ). For the adsorption kinetic experiments, approximately 150 g of porous
200 media (i.e., CG, CZ, FZ) were placed in glass bottles (volume 750 mL) containing 0,5 L
201 of 10 mg/L fluometuron solution. The bottles were placed in a thermostatic chamber at
202 20 ^{o}C and continuously shaken. In total, 90 bottles were prepared (30 bottles for each
203 substrate). At a specific time of 4, 8, 14, 24, 36, 48, 72, 96, 120, 144 hours, a bottle of
204 each porous media was taken and the fluometuron concentration in the solution was
205 measured.

206 Adsorption isotherm experiments were conducted for CZ and FZ. As in the case of
207 adsorption kinetic experiments, 150 g of porous media (i.e., coarse and fine zeolite) were
208 placed in 750 mL glass bottles containing 500 mL of a solution with different initial
209 fluometuron concentrations (2, 4, 8, 16 and 32 mg/L). These experiments were conducted
210 at 15 ^{o}C and 20 ^{o}C. On day 3 which was considered as the threshold, water samples were
211 taken and the fluometuron concentration in the solution was measured. The amount of
212 fluometuron adsorbed at equilibrium was calculated using the following equation:

213 $$q_e = \frac{(C_i - C_e)}{M} V \quad (1)$$

214 where: q_e (µg/g) is the adsorption capacity at equilibrium; C_i and C_e (mg/L) are the initial
215 and equilibrium concentrations of fluometuron in the solution, respectively; V (L) is the
216 volume of solution; and M (kg) is the mass porous media.

217 *Adsorption kinetic simulation*: The experimental data collected from the adsorption
218 kinetic experiments were fitted to the pseudo-first-order and pseudo-second-order
219 adsorption kinetic models (Ho and McKay 1998; Foo and Hameed 2010) to assess the

kinetic order of fluometuron adsorption process. These models are described by the equations (2) and (3), respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2 t} \quad (3)$$

where: q_t (mg/kg) is the amount of fluometuron adsorbed at time t (h); k_1 (1/h) and k_2 (kg/(mg h)) are the constant rates in pseudo-first and pseudo-second order equation, respectively.

Adsorption isotherm simulation: Two isotherm models, Langmuir and Freundlich, were used to simulate the adsorption isotherms of each porous media (i.e., CZ and FZ) used in the fluometuron adsorption experiments. The Langmuir isotherm model assumes monolayer coverage of the adsorbate over a homogenous adsorbent surface (Langmuir 1918), and the Freundlich isotherm assumes that the adsorption may be multilayered due to the heterogeneity of the surface charges (Freundlich, 1906). The linear form of Langmuir and Freundlich models are described by the Equations (4) and (5), respectively:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L q_m} \quad (4)$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (5)$$

where: q_m (mg/kg) is the theoretical maximum sorption capacity; q_e (mg/kg) is the amount of fluometuron adsorbed at equilibrium; C_e (mg/L) is the equilibrium concentrations of fluometuron in the solution; and k_L (L/mg) is the Langmuir energy sorption constant; k_F (mg/kg) is the Freundlich adsorption capacity constant; and n the intensity of adsorption constant. The n value determines the type of adsorption as follows: if the n value is equal

242 to one (n=1), the adsorption is linear; if the value is less than one (n<1), the adsorption
243 process is chemical; if the n value is greater than one (n>1), the adsorption is a favorable
244 physical process (Aljeboree et al. 2017; Kumar et al. 2010).
245
246 **2.5 Statistical analyses**
247
248 Nonparametric tests were used to determine differences in mean removal efficiencies of
249 fluometuron among the filter units, because the majority of data failed to meet the
250 assumption of normality and/or homogeneity. More specifically, the Kruskal-Wallis test
251 was used to investigate the effect of substrate and HRT on unit removal capacity. When
252 the difference between removal values was significant, the Mann–Whitney U test was
253 carried out to evaluate pair comparisons. Moreover, in order to assess the effect of feeding
254 way (batch or continuous) on filter units capacity, the Mann-Whitney U test was applied.
255 Statistical analyses were performed using SPSS 25.0 statistical package for Windows.
256
257 **3 Results and discussion**
258
259 **3.1 Adsorption kinetics and isotherms**
260
261 *Fluometuron adsorption kinetics:* Figure 2 presents the adsorption of fluometuron (q_t) at
262 various porous media and different contact times. In the first 24 hours, the adsorption rate
263 of the fluometuron increased rapidly but it gradually decreased with the increase in
264 contact time, until fluometuron adsorption reached equilibrium finally on day 3 (72
265 hours). The initial faster rate may be ascribed to the availability of the uncovered surface

266 area of the adsorbents (Shi et al. 2013). The best fit model was based on both the
267 calculated q_e values and correlation coefficient (R^2). Table 2 presents the experimental
268 adsorption capacity of fluometuron at equilibrium onto the three substates (i.e., CG, CZ
269 and FZ) and the kinetics parameters of adsorption of fluometuron according to pseudo-
270 first order and pseudo-second order models. The pseudo-first-order rate constant (k_1) and
271 the value of q_e were calculated from the plot of log (q_e-q_t) versus t (Equation 2) whereas
272 the pseudo-second-order rate constant (k_2) and the value of q_e were calculated from the
273 linear plot of $1/q_t$ versus 1/t (Equation 3).

274 According to results, the adsorption capacity of fluometuron onto fine-grade zeolite
275 was higher (more than double) than that of coarse-grained zeolite (Figures 2b,c; Table 2).
276 This is attributed to its higher specific surface area which increased the external surface
277 adsorption (Huang et al. 2010). Other relevant studies have reported that grain size
278 affected the amount of NH_4-N adsorbed on zeolite, with smaller sized granules giving
279 better results (Wang et al. 2015). On the other hand, small zeolite grains (e.g., smaller
280 than 4 mm) may cause clogging when used as porous media in filters and constructed
281 wetlands (Kotoulas et al. 2019; Gikas et al. 2017). The ranking order of the fluometuron
282 adsorption capacity (Figure 2; Table 2) was: FZ > CZ > CC. The kinetic simulation results
283 showed that the pseudo-first order model was suitable for describing fluometuron
284 adsorption to all three tested porous media, in terms of higher correlation coefficient, R^2 >
285 0.96 (Table 2). Moreover, the q values calculated ($q_{e,\,cal}$) from pseudo-first order model
286 were very close to the experimental q values ($q_{e,exp}$) in comparison to those calculated
287 from the pseudo-second order model (Figure 2; Table 2). These results indicated that the
288 pseudo-first order model provided a better correlation for the fluorometer adsorption on
289 all three porous media tested compared to the pseudo-second order model.

290 *Fluometuron adsorption isotherm:* Langmuir and Freundlich models were used in
291 order to describe the equilibrium adsorption isotherms and to investigate the maximum
292 adsorption capacity of the two porous media (i.e., CZ and FZ) toward fluometuron at two
293 temperatures (i.e., 15 and 20 ^{o}C). The results presented in Figure 3 demonstrate that the
294 adsorption of fluometuron depended on the concentration and temperature. Highest
295 adsorption capacity was recorded at temperature of 20 ^{o}C for the two tested porous media.
296 The values of q_m and k_L of the Langmuir isotherm as well as the values of 1/n and k_F of
297 the Freundlich isotherm were obtained from the Equations (4) and (5), respectively, and
298 are presented in Table 3. The best fit model was based on the linear regression correlation
299 coefficient (R^2). The results showed that fluometuron adsorption capacities were better
300 fitted to the Freundlich model, which indicated higher R^2 values for both CZ and FZ
301 (Table 3). In addition, in all cases the 1/n value was less than 1, indicating that
302 fluometuron adsorption on both media is a favorable physical process at experimental
303 conditions.
304
305 **3.2 Influent and effluent physicochemical parameters of wastewater**
306
307 Table 4 presents statistics, such as mean, standard deviation (SD), minimum and
308 maximum of physicochemical parameters in influent and effluent fluometuron solution
309 of the three batch-feeding filters (i.e., CG-B, CZ-B and FZ-B) and of the three continuous-
310 feeding filters (i.e., CG-C, CZ-C and FZ-C). The temperature values showed very small
311 differences between the influent and effluent water of the six filter units and varied
312 between 21.6 ^{o}C and 29.1 ^{o}C. The mean pH values were slightly increased in all of the
313 filters and tended to be kept in the neutral or slightly alkaline zone. The pH values ranged
314 from 7.2 to 7.4 and from 7.3 to 7.7 in influent and effluent water, respectively, indicating

315 that there was no significant change throughout the monitoring period (Table 4).
316 Regarding the DO, its mean concentration in the influent water was 7.0 mg/L and
317 decreased in the filter units probably due to the consumption by microorganisms. In batch
318 loading filters, the reduction was greater compared to those with continuous loading.
319 More specifically, the percentages of reduction in batch filters CG-B, CZ-B and FZ-B
320 were 52.1%, 56.6% and 48.5%, respectively. In continuous feed filters the percentages
321 reduction for CG-C, CZ-C and FZ-C were 36.9%, 40.2% and 35.0%, respectively. Table
322 4 shows the mean EC values slightly increased in both batch and continuous feeding
323 filters with substrates CG and CZ. Higher increases in mean EC values of 7.6% and 14.3%
324 were observed in the FZ-B and FZ-C filters, respectively, probably due to the interactions
325 between water and fine zeolite which led to the release of salts into the fluid, resulting in
326 the increase of EC values.
327
328 ***3.3*** **Overall performance statistics**
329
330 Table 5 presents the concentration of fluometuron in influent and effluent for batch and
331 continuous feeding in the six filter units. Figure 4 shows the removal rate (%) of
332 fluometuron in the filter units. The mean influent concentrations of fluometuron varied
333 from 39.3 mg/L to 39.6 mg/L for both batch and continuous feeding filters throughout the
334 entire experimental period. The mean effluent concentrations of fluometuron of the CZ-
335 B and CZ-C filters for HRT of day 1 were 33.6 mg/L and 33.0 mg/L, respectively, and
336 higher than those of the other filters. On the other hand, the lower mean concentrations
337 of 26.2 mg/L and 26.1 mg/L were measured in the FZ-B and FZ-C filters, respectively,
338 for HRT of 4 days (Table 5). Regarding the removal efficiency of the fluometuron, higher

339 performance was noticed in the FZ-C unit at HRT of 2 days and 4 days, which resulted
340 in removal of 34.2% for both HRT. Lower removal performance of 14.4% was observed
341 in CG-B filter at HRT of 1 day (Figure 4). For both feeding strategies (i.e., batch and
342 continuous), higher removal values were noticed at HRT of 4 days compared to the other
343 HRTs, indicating that the HRT is an important parameter and affects the efficiency of
344 pesticide treatment. In a comparison between the three porous media, higher fluometuron
345 removal was observed in the filters with FZ (fine zeolite). More specifically, the FZ-B
346 filter indicated better performance than CG-B and CZ-B, and the FZ-C filter indicated
347 better performance than CG-C and CZ-C filters (Figure 4). These results reveal that
348 porous media are also an important design parameter in gravity filters.

349 There are various processes for pesticides elimination in aqueous environment, but
350 the most important processes are photolysis, volatilization, hydrolysis, oxidation and
351 microbial degradation (Lopez et al. 2014). In addition, pesticides are removed in gravity
352 filters by absorption on porous media. Photolysis is a process by which various pesticides
353 are degraded into other simpler compounds. Direct photolysis is possible when the
354 considered pesticide absorbs sunlight. However, Halladja et al. (2007) noted that
355 fluometuron poorly absorbs solar light, whereas Lam et al. (2005) reported direct
356 photolysis with simulated solar light (k>290 nm). Given the above and the experimental
357 conditions of the present study, the fluometuron removal in the filter units is considered
358 negligible.

359 Volatilization has been reported by various researchers (Page et al. 2010) as another
360 important mechanism for the loss of chemicals such as pesticides from soil and water.
361 However, the removal of fluometuron from surface water by volatilization is not expected
362 to be significant due to the low value of the Henry's law constant (2.63×10^{-4} Pa m^3/mole;

363 Table 1), which is less than 0.1 Pa m^3/mole, thus fluometuron is characterized as non-
364 volatile (PPDB, 2016). In addition, fluometuron is not expected to volatilize from dry soil
365 surfaces based upon a vapor pressure of $9.38x10^{-7}$ mm Hg (Table 1) (PPDB 2016). In the
366 case of gravity filters, there is no water on porous media surface and, as mentioned before,
367 throughout the experiment the containers (filters) were closed, therefore, the elimination
368 of fluometuron by volatilization is considered negligible. The hydrolysis half-life of
369 fluometuron in water is 2.4 years at pH 5 and 2.8 years at pH 9 (Worthing, 1987; NCBI,
370 2021). Therefore, hydrolysis of fluometuron in water is not expected to be a significant
371 degradation route.
372 According to Mueller et al. (1992), biodegradation is a process in which fluometuron
373 is lost in most soils. Depending on the type of soil and climatic conditions, the half-life
374 of fluometuron degradation ranged from 62.5 to 117 days with an average value of 89.8
375 days (Table 1). Based on the above, fluometuron can be characterized as moderately
376 persistent, as its degradation in soil lasts between 30 and 100 days (PPDB, 2016).
377 Moreover, biodegradation is favored by the increase of organic matter in the soil (Locke
378 et al. 2007). According to Shankle et al. (2004), fluometuron sorption was higher in
379 wetland soils than in field soils, and this was attributed to increased organic matter. Given
380 the conditions of the experiment in the present work, the removal of fluometuron by
381 biodegradation is considered negligible because there is no organic matter in the filter
382 units. In view of the above, it can be seen that the decrease of fluometuron concentration
383 at the outlet of the filter units is mainly due to its adsorption on the porous media.
384
385 **3.4 Effect of feeding mode, porous media and hydraulic residence time**
386

Figure 5 presents box and whisker plots of fluometuron removal in the gravity filters with porous media and in relation to various design parameters such as the mode of loading (Figure 5a), the type of porous media (Figure 5b) and the hydraulic residence time (Figure 5c). The mean removal values of the herbicide for batch and continuous loading were 21.2% and 22.2%, respectively. The Mann–Whitney U test showed that there was no statistically significant difference between them ($p > 0.05$). These results indicate that there was no significant effect of the way the filters are fed on the removal of fluometuron. This fact should be taken into account in filters design for the agricultural runoff treatment from point and non-point sources of pollution.

As illustrated in Figure 5b, the filter units with porous media of FZ demonstrated better removal efficiency than the filters with porous media of CG and CZ. The mean percentages removal values were 16.6%, 20.0% and 28.6% for the filters with porous media of CG, CZ and FZ, respectively. The difference in the percentages of removal was due to the different in the adsorption capacities of fluometuron on the three porous media, which was discussed in section "Adsorption kinetics experiment". Statistical analysis indicated statistical significant (Kruskal-Wallis test: $p<0.001$) differences between the porous media in terms of percent removal of fluometuron. According to the Mann-Whitney U test, the removal of fluometuron in CG was significantly lower than those in CZ ($p<0.05$) and FZ ($p<0.05$), and there was no statistical significant difference between CZ and FZ ($p>0.05$).

According to Gikas et al. (2018b), HRT is an important parameter for pesticide removal in the constructed wetlands and increase in HRT results to increase pesticide dissipation in the wetland. The values of HRT for various pesticides ranged between 2 and 8 days, while further increase in HRT did not result in pesticide removal (Locke et

411 al. 2011; Papaevangelou et al. 2017; Gikas et al. 2018a, b). However, there is limited
412 published literature on natural systems (e.g., constructed wetlands, oxidation ponds, etc.)
413 regarding the treatment of water contaminated with fluometuron. In the present study,
414 throughout the entire experimental period, the mean removal values of fluometuron in
415 filter units were 17.1%, 23.5% and 24.4% for HRT of 1 day, 2 days and 4 days,
416 respectively (Figure 5c). The Kruskal-Wallis test indicated statistically significant
417 ($p<0.001$) differences between the HRT in terms of percent removal of fluometuron.
418 According to the Mann-Whitney U test, the removal of fluometuron in filter units at HRT
419 1 day was significantly lower than that at HRT 4 days ($p<0.05$), and there were no
420 significant differences between HRT of 1 day and 2 days ($p>0.05$), and between HRT 2
421 days and 4 days. In addition, Figure 4 shows that for all six filters the difference in
422 fluometuron removal between HRT of 2 days and 4 days was very small, ranging from
423 0% in the FZ-C to 2.4% in the CG-B filter. These results along with the results of the
424 adsorption kinetics experiment indicate that an HRT of 4 days may be sufficient for
425 fluometuron removal. This means that increasing the hydraulic residence time to more
426 than four days will not lead to an increased removal of fluometuron. The results of this
427 study could be particularly useful in the design of gravity filters (batch or continuous
428 feeding) used for treating the rinsing water of spraying machines and/or tanks, which are
429 rich in pesticide residues.
430
431 **4 Conclusions**
432
433 Filters with three different porous media, coarse gravel, coarse zeolite and fine zeolite,
434 were used in the removal of herbicide fluometuron from aqueous solution. Design and

operation parameters such as feeding way, porous media and HRT were investigated and fluometuron adsorption experiments were conducted. Regarding the kinetic and isotherm simulation, the adsorption experimental data fitted to the pseudo-first order model and the Freundlich model, respectively, and the highest fluometuron adsorption was recorded for fine zeolite. The FZ-C unit at HRT of 2-days and 4-days achieved the highest fluometuron removal (34.2%). According to the results of the present study, the filters feeding strategy (i.e., batch or continuous feeding) were found to have little effect on herbicide removal; the HRT is the most important parameter which affects the filter capacity in fluometuron removal. The removal of fluometuron could be increased by constructing a system of two or three filters in series.

Therefore, the filters can be considered an effective and practical management measure for the treatment of water which is contaminated by pesticides due to: (a) the low construction and operation cost; (b) the absence of mechanical parts, and therefore, no demand for specialized personnel. The construction and operation of filters at the sites where the spray solutions are prepared and the spraying machines and tanks are washed is recommended, in order to accept and treat the contaminated water that results from the above processes. Extending research to filters with other porous media and other chemical classes of pesticides is considered necessary. Finally, the porous media examined in this study can also be used as substrates in constructed wetlands.

Declarations

Ethics approval and consent to participate: Not applicable.

Consent for publication: Not applicable.

Availability of data and materials: The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests: The authors declare that they have no competing interests.

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Authors' contributions: Georgios D. Gikas and Zisis Vryzas contributed to the study conception and design. Material preparation, data collection and analysis were performed by all authors. The first draft of the manuscript was written by Georgios D. Gikas. Zisis Vryzas commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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FIFURE CAPTIONS

Fig. 1. Schematic layout of filter units: (a) batch feeding; (b) continuous feeding.

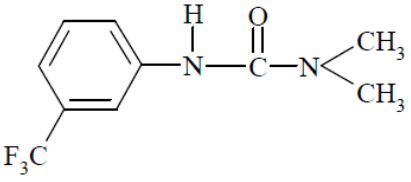
Fig. 2. Fluometuron adsorption on porous media: (a) coarse gravel; (b) coarse zeolite; (c) fine zeolite.

Fig. 3. Isotherm equations (Langmuir and Freundlich) fitted for fluometuron adsorption on: (a) coarse zeolite (CZ) and (b) fine zeolite (FZ).

Fig. 4. Removal rate (%) of fluometuron in filter units.

Fig. 5. Box-whisker plots of fluometuron removal in filter units and effect of design parameters: (a) loading; (b) substrate; (c) hydraulic residence time (HRT). The line inside the box denotes median values, the upper box frame the 75 percentile and the lower box frame the 25 percentile and the whiskers the max and min values.

668 **Table 1.** Physicochemical properties of fluometuron (PPDB 2016).

Parameter	Value
Molecular formula	$C_{10}H_{11}F_3N_2O$
Substance group	Phenylurea
Structural formula	
Molecular weight (g/mol)	232.20
Water solubility at 20 °C (mg/L)	111.0
Octanol-water partition coefficient (25ºC) $LogK_{ow}$	2.38
Vapour pressure at 25 °C (mmHg)	$9.38x10^{-7}$ (low volatility)
Sorption coefficient K_{oc} (L/kg)	30.8-117.0
Henry's Law constant at 22-25 ºC (Pa m^3/mol)	$2.63x10^{-4}$
Soil degradation DT_{50} (field)[1] (days)	89.8

[1] *half-life for field studies*

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674 **Table 2.** Comparison of the pseudo-first order and pseudo-second order reaction rate
675 constants for various tested porous media.

Porous media	$q_{e,exp}$ (mg/kg)	Pseudo-first order model			Pseudo-second order model		
		$q_{e,cal}$ (mg/kg)	k_1 (1/h)	R^2	$q_{e,cal}$ (mg/kg)	k_2 (kg/(mg h))	R^2
CG	1.55	1.68	0.025	0.96	3.65	0.001	0.94
CZ	5.22	4.98	0.140	0.98	8.23	0.004	0.95
FZ	12.26	12.46	0.068	0.99	16.23	0.003	0.98

$q_{e,exp}$= experimental adsorption capacity at equilibrium
$q_{e,cal}$= calculated adsorption capacity at equilibrium

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683 **Table 3.** Adsorption isotherm parameters for coarse (CZ) and fine zeolite (FZ).

Porous media	T (°C)	Langmuir isotherm			Freundlich isotherm		
		q_m (mg/kg)	K_L (L/mg)	R^2	1/n	K_F (mg/kg)	R^2
CZ	15	3.67	1.29	0.73	0.21	2.13	0.87
	20	5.37	0.70	0.71	0.31	2.29	0.95
FZ	15	4.74	0.18	0.84	0.53	0.86	0.96
	20	16.55	0.06	0.96	0.63	1.39	0.97

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694 **Table 4.** Statistics of influent and effluent values of physicochemical parameters in the

695 filter units for the entire experimental period.

Parameter		Filter influent	Filter effluent					
			Batch-feeding			Continuous-feeding		
			CG-B	CZ-B	FZ-B	CG-C	CZ-C	FZ-C
T (°C)	Mean	23.4	26.2	25.1	24.6	24.5	23.6	23.5
	SD	2.6	2.4	2.3	2.3	1.8	1.7	1.8
	Min	21.2	22.4	22.0	22.1	22.0	21.7	21.6
	Max	28.7	29.1	27.9	28.2	27.1	25.9	26.1
pH	Mean	7.3	7.5	7.4	7.4	7.5	7.5	7.4
	SD	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Min	7.2	7.4	7.4	7.3	7.4	7.4	7.3
	Max	7.4	7.6	7.5	7.6	7.7	7.6	7.6
DO (mg/L)	Mean	7.0	3.4	3.0	3.6	4.4	4.2	4.6
	SD	0.4	0.3	0.3	0.3	0.3	0.1	0.3
	Min	6.1	2.8	2.7	3.1	4.0	4.1	4.1
	Max	7.5	3.8	3.4	4.1	4.9	4.4	5.0
EC (μS/cm)	Mean	526	537	540	566	529	527	601
	SD	5.2	11.1	10.1	17.1	18.1	10.5	53.7
	Min	519	522	520	545	496	500	545
	Max	535	556	551	601	558	530	679

CG-B, CZ-B, FZ-B are the batch-feeding filter units; CG-C, CZ-C, FZ-C are the continuous-feeding filter units

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Table 5. Statistical data of influent and effluent concentrations of fluometuron in filter units

	Influent concentration (mg/L)			Effluent concentration (mg/L)								
				Batch feeding								
				CG-B			CZ-B			FZ-B		
	1 d	2 d	4 d	1 d	2 d	4 d	1 d	2 d	4 d	1 d	2 d	4 d
Mean	39.3	39.3	39.6	33.6	33.2	32.6	32.7	31.2	31.0	31.9	26.8	26.2
SD	1.3	0.2	0.6	0.7	0.2	0.1	0.9	0.7	0.2	1.2	0.9	0.4
				Continuous feeding								
				CG-C			CZ-C			FZ-C		
	1 d	2 d	4 d	1 d	2 d	4 d	1 d	2 d	4 d	1 d	2 d	4 d
Mean	39.3	39.3	39.6	33.0	32.5	32.5	32.7	30.6	30.5	31.9	25.9	26.1
SD	1.3	0.2	0.6	1.4	0.3	1.9	0.7	1.5	0.1	0.1	0.2	0.2

1 d, 2 d, 4 d: periods of respective HRT (days); SD: standard deviation

Figures

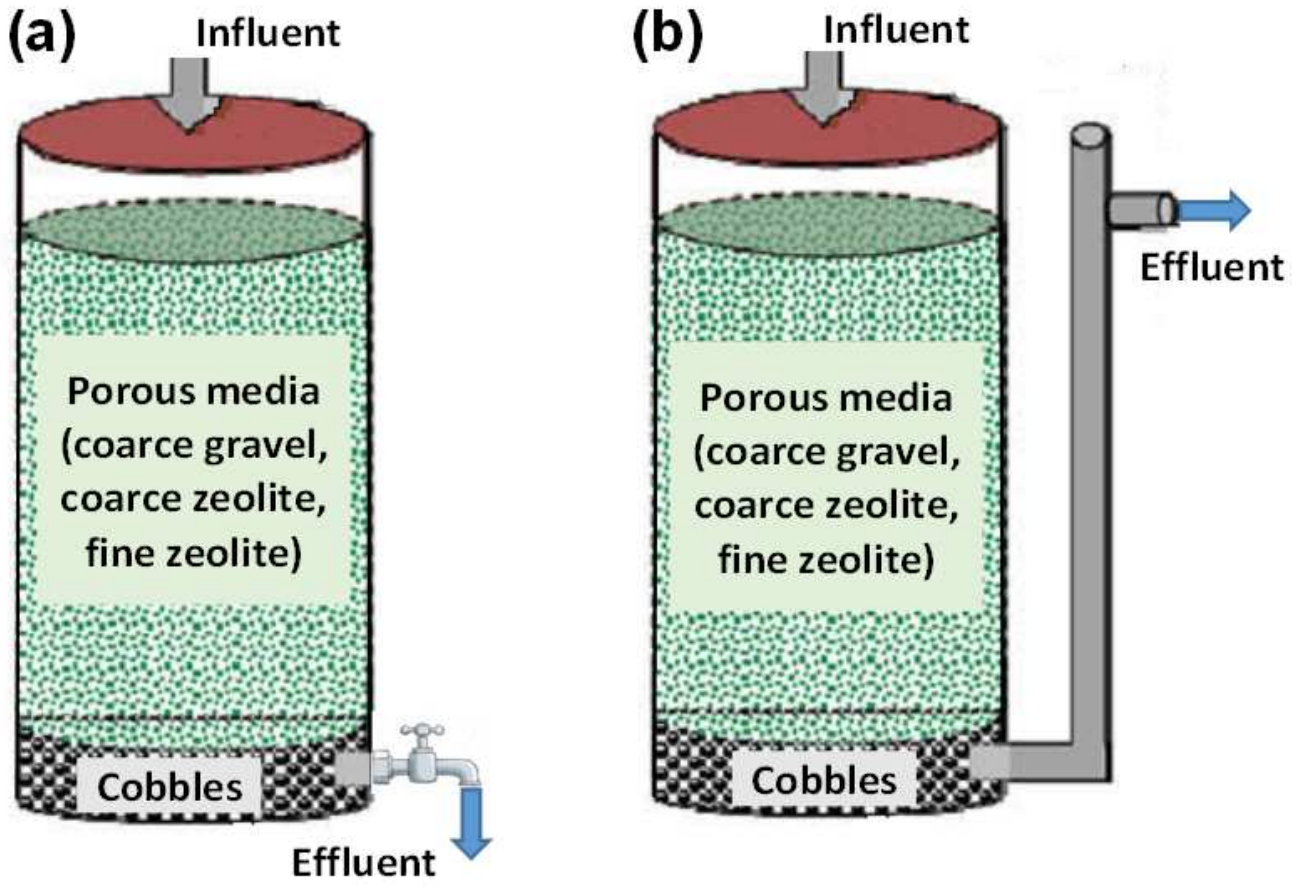

Figure 1

Schematic layout of filter units: (a) batch feeding; (b) continuous feeding.

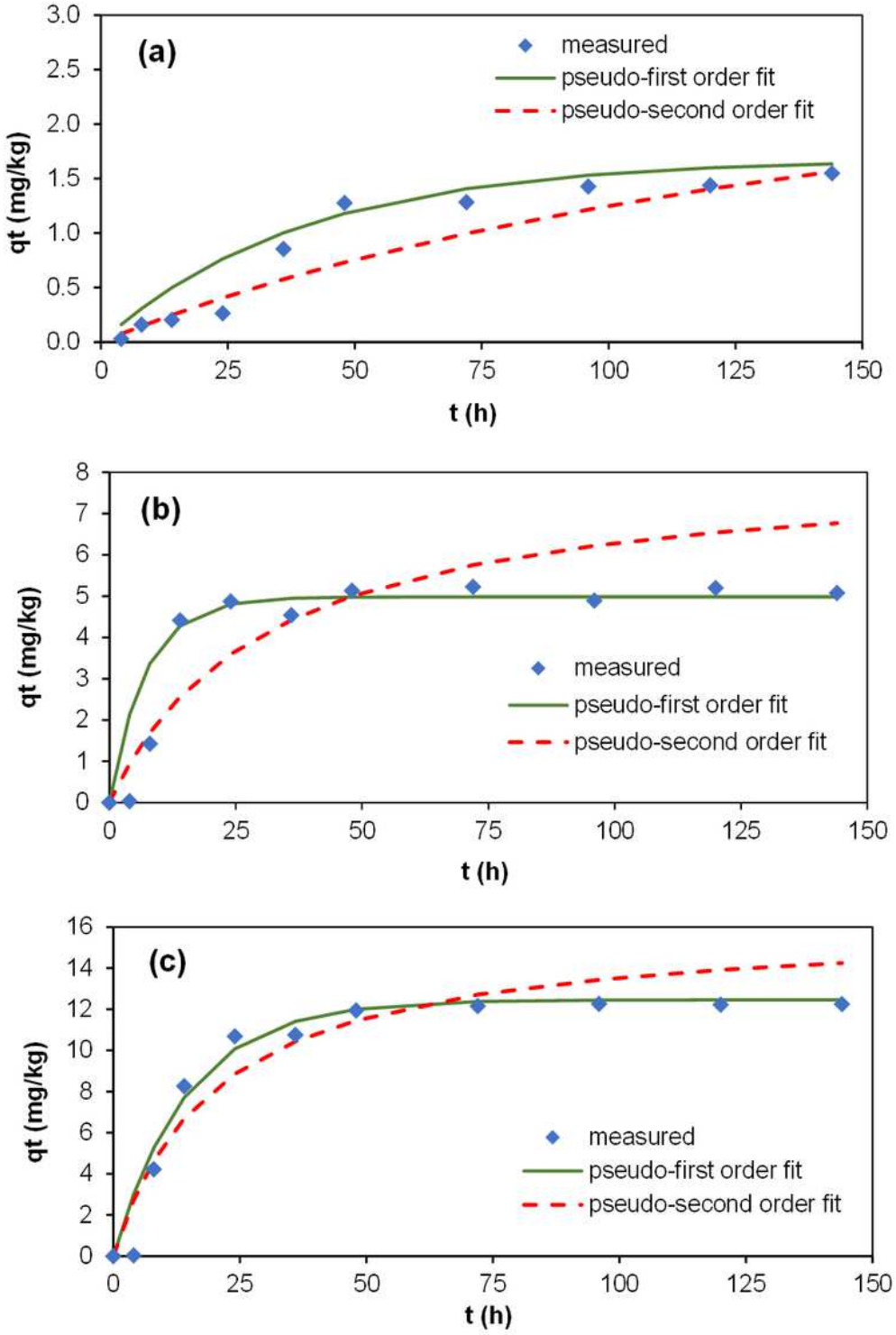

Figure 2

Fluometuron adsorption on porous media: (a) coarse gravel; (b) coarse zeolite; (c) fine zeolite.

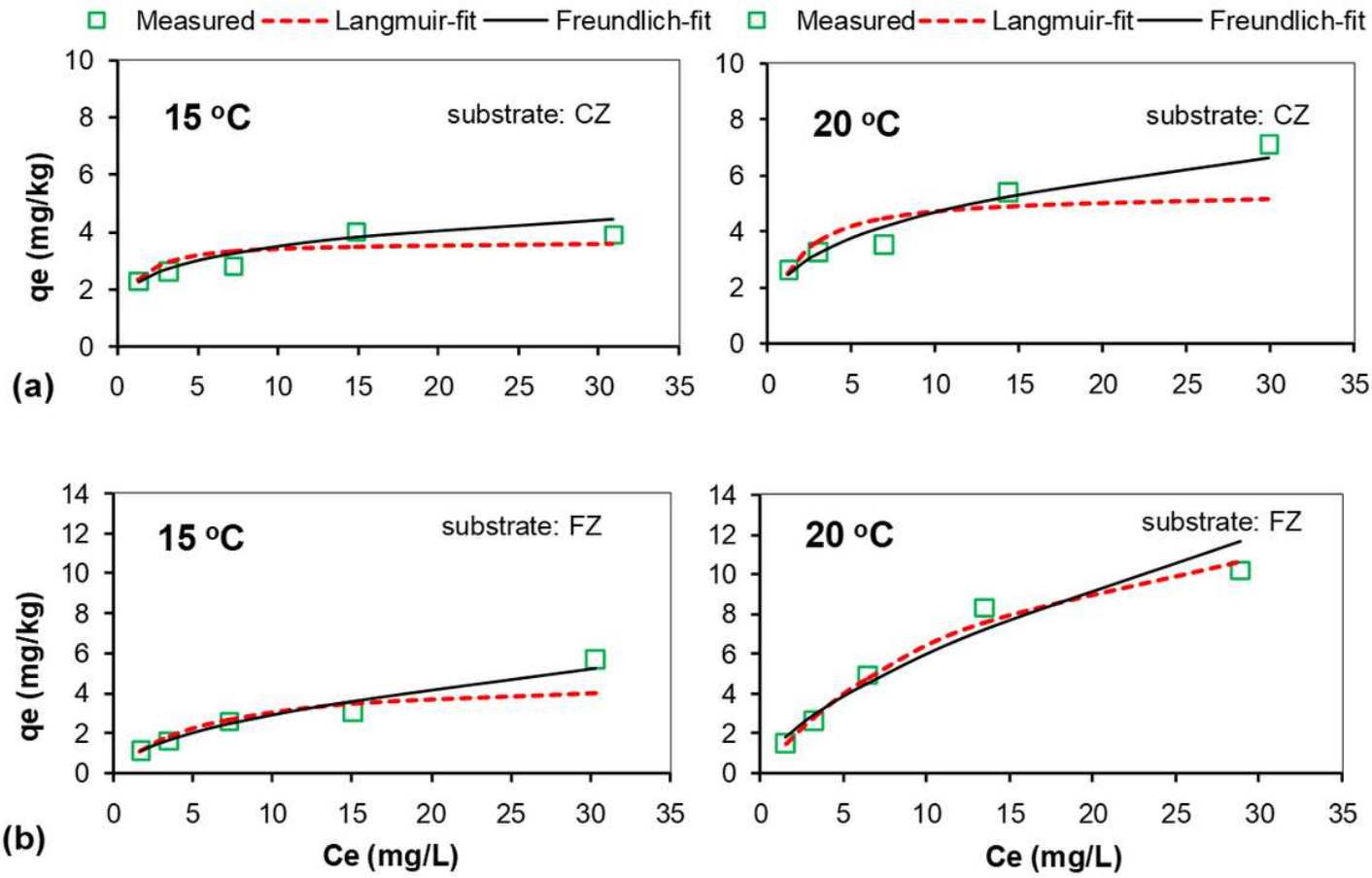

Figure 3

Isotherm equations (Langmuir and Freundlich) fitted for fluometuron adsorption on: (a) coarse zeolite (CZ) and (b) fine zeolite (FZ).

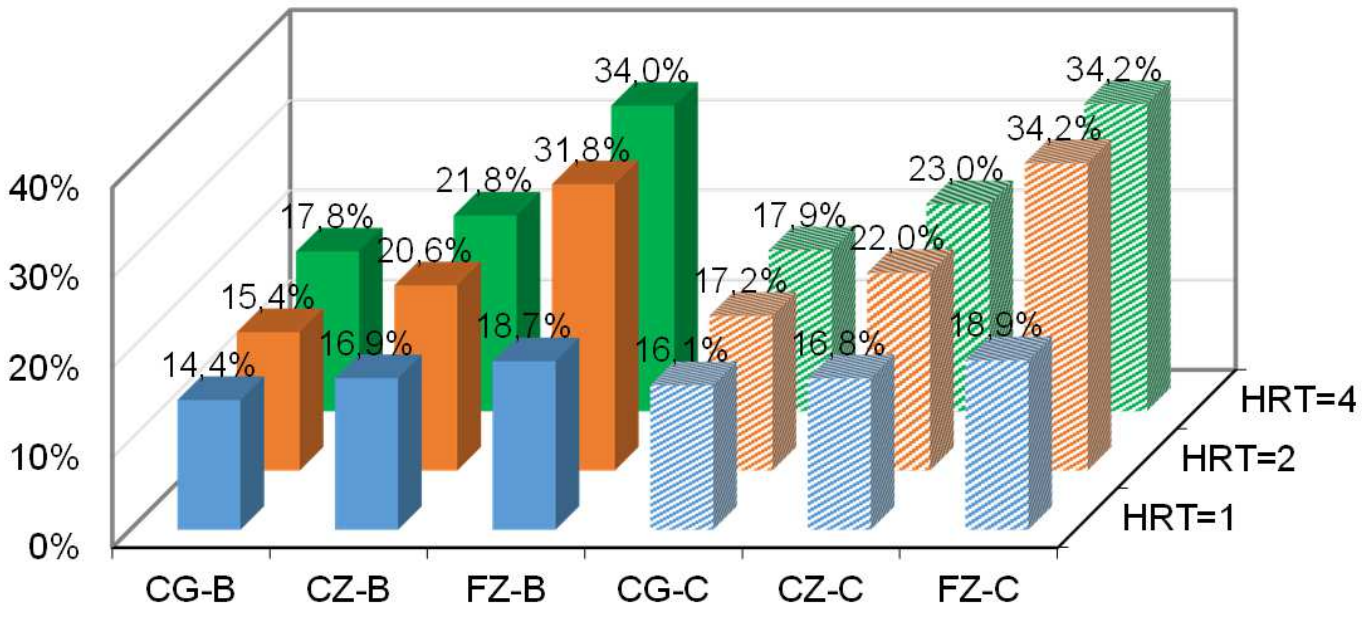

Figure 4

Removal rate (%) of fluometuron in filter units.

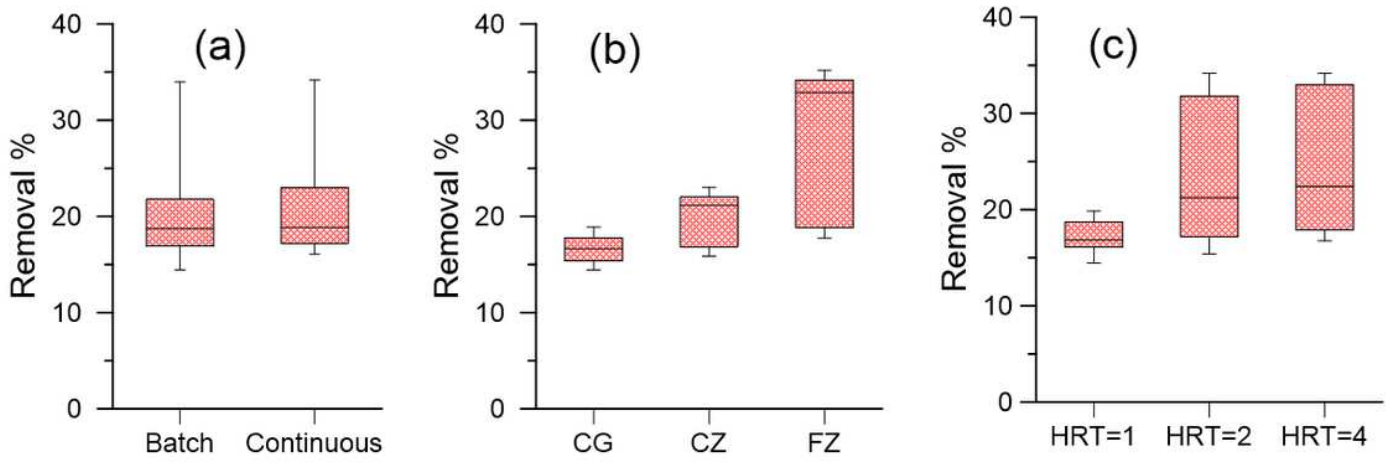

Figure 5

Box-whisker plots of fluometuron removal in filter units and effect of design parameters: (a) loading; (b) substrate; (c) hydraulic residence time (HRT). The line inside the box denotes median values, the upper box frame the 75 percentile and the lower box frame the 25 percentile and the whiskers the max and min values.