

# Efficient removal of antibiotics from water via aqueous portlandite carbonation

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Renard

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1	Efficient Removal of Antibiotics from Water via Aqueous							
2	<b>Portlandite Carbonation</b>							
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#### 18 Abstract

19 Current wastewater treatment technologies struggle to remove antibiotics from wastewaters, leading to contamination of surface and groundwater. Therefore, more effective and efficient 20 processes for removing antibiotics from water are needed. The present study reports for the first 21 22 time that three widely used antibiotics (amoxicillin, ceftriaxone, cefazoline) can be successfully removed from water under ambient conditions by using aqueous carbonation of portlandite. 23 Breakthrough curves acquired from flow-through experiments and their respective removal 24 isotherms were mainly used to determine quantitative equilibrium parameters. In this way, the 25 removal of antibiotics using aqueous portlandite carbonation is very efficient for amoxicillin (9.5 26 27 mg/g), followed by cefazoline (4.3 mg/g) and ceftriaxone (2.7 mg/g). In a comparison perspective, nanomagnetite-interfacial Fenton reaction is more effective in removing amoxicillin (76.5 mg/g); 28 29 however, the process is slower and chemically more complex. However, both investigated methods offer promising results at the laboratory scale and are technically feasible to be implemented in 30 conventional and/or advanced wastewater treatment plants. 31

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- 41 Keywords: Antibiotic, Removal, Wastewater, Carbonation, Portlandite, Magnetite, Flow-through
- 42 curves, Isotherms

#### 43 **1. Introduction**

De novo designed organic molecules, including pharmaceuticals, hormones, personal care 44 products, surfactants, drugs, and pesticides, are a serious source of contaminants in water. Among 45 these pollutants are antibiotics, the most frequently prescribed drug of modern human medicine, 46 which are also widely used in the animal farming industry, including cattle, swine, poultry, and 47 fish. The benefits of antibiotics in healthcare of human and animals are undisputed. However, 48 49 excessive and wrong usage raises the risk of drug resistance in the environment, leading to the most common antibiotics being no longer effective in controlling infectious diseases [1-5]. Antibiotics 50 from different sources (e.g. municipal waste water, hospitals, animal production, and 51 52 pharmaceutical industries) are ultimately discharged into wastewater treatment plants. However, conventional and advanced treatment plants are not effective in removing antibiotics leading to the 53 release of these compounds in surface and groundwater [6-7]. In the last two decades, various 54 methods to remove and/or degrade antibiotics from water have been investigated in the laboratory 55 and frequently tested in pilot or plant scale, including biodegradation, nanofiltration, advanced 56 57 oxidation processes, photocatalytic degradation, reverse osmosis, ozonation and adsorption [8-15]. Among these methods, adsorption appears to be a suitable technique to remove various antibiotics 58 from contaminated water and industrial effluents because of its high efficiency, simple design, easy 59 60 operation and its ability to remove a wide range of contaminant concentrations. High specific surface areas (>500  $\text{m}^2/\text{g}$ ) and microporous materials (e.g. metal–organic frameworks – MOFs) are 61 62 frequently required; but in general, diversified natural or synthetic materials (including green and low-cost materials) have been tested to remove antibiotics [16-18]. Mineral precipitation has also 63 been suggested as an economic and robust method to remove ionic and organic pollutants from 64 water; for example, calcite precipitation can remove several heavy metals and metalloids from 65

66 water, but rarely organic pollutants [19-20].

In the present study we show that calcite precipitation via aqueous portlandite carbonation 67  $(Ca(OH)_2 + CO_2 \Rightarrow CaCO_3 + H_2O)$  in a flow-through reactor at ambient conditions is a simple 68 method to effectively remove three types of antibiotics (amoxicillin, ceftriaxone and cefazolin). 69 This carbonation method has been investigated in order to produce nanosized calcite under mild 70 71 and hydrothermal conditions or in order to sequester ionic pollutants from water [19-20]. In this way, based on breakthrough curves and respective sequestration isotherms we establish the 72 73 efficiency of this approach. In addition, we show, using the same flow-through setup, that a Fentontype oxidation reaction using magnetite nanoparticles is also an efficient process to remove 74 amoxicillin. However, this oxidation reaction requires low pH (pH<3), a significant amount of 75 76 oxygenated water and a ferrous source (Fe(II) as enhancing reaction agents.

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#### 78 2. Materials and Methods

#### 79 *2.1. Chemicals*

(amoxicillin ( $C_{16}H_{19}N_3O_5S$ ), erythromycin ( $C_{37}H_{67}NO_{13}$ ), 80 Four antibiotics ceftriaxone 81 (C18H18N8O7S3), cefazolin (C14H14N8O4S3)) and soluble salts (calcium chloride dihydrate 82 (CaCl<sub>2</sub>.2H<sub>2</sub>O), ferrous chloride dihydrate (FeCl<sub>2</sub>.2H<sub>2</sub>O), ferric chloride heptahydrate (FeCl<sub>3</sub>.6 83 H<sub>2</sub>O) and sodium hydroxide (NaOH)) with high purity (>99%) were obtained from Sigma-Aldrich. 84 All reactants were used as received. Carbon dioxide (CO<sub>2</sub>) was obtained from Linde Gas S.A. with 85 99.995% of chemical purity. This gas was used as received and directly bubbled into the antibiotic 86 inlet solutions. Deionized water (18.2 M $\Omega$  of resistivity) used in the synthesis of minerals, drinking water of the city of Grenoble (its ionic composition and/or chemistry was already reported in a 87 previous study [21]) used in flow-through and batch experiments and oxygenated water (H<sub>2</sub>O<sub>2</sub>) at 88 - 5 -

30% (provided by Sigma-Aldrich) and chloride acid (HCl) at 10% (provided by Sigma-Aldrich)
used in the Fenton's reaction.

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92 *2.2. Minerals* 

Portlandite platy nanoparticles (Ca(OH)<sub>2</sub> with hexagonal shape and with 16 m<sup>2</sup>/g of specific surface area) were synthesized using a coprecipitation method in alkaline medium (Ca<sup>2+</sup> + 2OH<sup>-</sup>  $\Rightarrow$ Ca(OH)<sub>2</sub>) by rapid mixing of 100 ml of calcium chloride solution (1 M) with 210 ml of sodium hydroxide (1 M) at room temperature. The resulting suspension was stirred for 15 minutes and then the precipitate was recovered by filtration and washed with deionized water. Finally, the portlandite was dried in a CO<sub>2</sub>-free atmosphere at 60 °C for 24 h.

Magnetite spherical nanoparticles (Fe<sub>3</sub>O<sub>4</sub> with size<20nm, with 28 m<sup>2</sup>/g of specific surface area) were synthesized using a coprecipitation method by adding 200 ml of a mixed-valent iron solution (1 M, (Fe<sup>2+</sup> + Fe<sup>3+</sup>), pH ~ 1) with a controlled flow rate (2.3 ml/min) to 200 ml of NaOH solution (4 M, pH = 14) at room temperature under constant stirring. The reaction mechanism and kinetics for this coprecipitation reaction have been previously investigated by time-resolved Raman spectroscopy [22].

105 Calcite nanoparticles (CaCO<sub>3</sub> with size<100nm, with 9 m<sup>2</sup>/g of specific surface area) was 106 synthesized by aqueous carbonation of portlandite with compressed CO<sub>2</sub> (55 bar) at room 107 temperature, following the overall reaction: Ca(OH)<sub>2</sub> + CO<sub>2</sub>  $\Rightarrow$  CaCO<sub>3</sub> + H<sub>2</sub>O. The mineral 108 composition, kinetics, and reaction mechanisms were determined by time-resolved Raman 109 spectroscopy measurement [23].

#### 111 2.3. Flow-through reactor experiments

112 Aqueous carbonation of portlandite: Two flow-through reactors with 50 mL internal volume were first filled with Grenoble drinking water, ionic composition reported in Hajji et al. [21]. One reactor 113 114 also contained 1 g of synthetic portlandite (reactive tracer reactor). The other reactor without 115 mineral-reactant was used as a reference (inert tracer reactor). An antibiotic-rich solution (2 L with 100-120 mg/L of a given antibiotic) was constantly bubbled with  $CO_2$  in a beaker. Then, this  $CO_2$ -116 117 saturated antibiotic solution was simultaneously percolated through both reactors at a constant rate of 12.2 mL/min for 80 minutes at room temperature (20 °C). The mineral-solution suspension in 118 119 the flow-through reactor was continuously stirred using a magnetic Teflon bar. The outflow 120 solutions from the inert and reactive tracer reactors were filtered in situ through 0.2 µm pore size Teflon membranes located on the top of the reactors. The antibiotic concentration in filtered 121 solutions at various times of the experiment (0.5, 2, 5, 10, 15, 20, 80 minutes) were determined 122 with Ultraviolet-Visible (UV-Vis) spectroscopy (Agilent Cary 60). We used calibration lines for 123 amoxicillin (C<sub>amoxicillin</sub>=A/0.0216) at 228 nm (where C is concentration and A is the absorbance), 124 ceftriaxone (C<sub>ceftriaxone</sub>=A/0.0444) at 237 nm and cefazolin (C<sub>cefazolin</sub>=A/0.0236) at 273nm. These 125 measurements were used to determine experimental breakthrough curves for the solutions of the 126 inert and reactive tracer reactors, as previously described for As and Cr sequestration by using 127 128 nanostructured synthetic minerals [21]. All experiments were repeated at least two times in order to confirm their reproducibility. 129

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*Fenton reaction*: The same experimental setup as described above was used to investigate the oxidation process of amoxicillin. Here, 1 g of magnetite nanoparticles was placed in the reactive tracer reactor and provided a ferrous iron source for the Fenton reaction at the magnetite-solution

interfaces. The inlet solution containing amoxicillin (2 L with 120 mg/L) was modified to activate the Fenton reaction by adding 1.2 ml of 30% oxygenated water ( $H_2O_2$ ) and adjusting the pH to 2.6 by adding HCl. This solution was simultaneously flown through both (inert and reactive) reactors at a rate of 2.3 ml/min during 7 hours. Solution samples were retrieved at different time intervals (outlet solutions from inert and reactive tracer reactors) and analyzed by UV-Vis spectroscopy in order to measure the evolution of the amoxicillin concentration and determine the respective breakthrough curves.

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Calculation of removal isotherms: The experimental breakthrough curves obtained from the inert 142 143 and reactive tracer reactors were used to determine the removal isotherm for a given antibiotic. The corresponding removed fraction between C=0 and  $C_i$  was calculated by integrating the surface area 144 between the breakthrough curves of the inert and reactive tracers inside of a given interval of time. 145 Each of these calculations provided one point  $(C_i, q_i)$  of the isotherm; assuming an equilibrium 146 concentration in each point as explained in Limousin et al. [24]. The relationship to determine the 147 removed amount  $(q_i=q_e)$  for a given equilibrium concentration  $(C_i=C_e)$  from breakthrough curves 148 writes as follows: 149

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$$q_{i} = \frac{\text{Flow rate}}{\text{Solid mass}} A_{i} = \frac{\text{Flow rate}}{\text{Solid mass}} \left( \int_{t=0}^{t=t_{i}} C_{\text{inert tracer}} \, dt - \int_{t=0}^{t=t_{i}} C_{\text{reactive tracer}} \, dt \right)$$
(1)

The main advantage of this method is that only one percolation experiment for inert and reactive tracer reactors is required to determine one isotherm for a given pollutant. Finally, all removal isotherms obtained from breakthrough curves were fitted using Hill's model ( $q_e = \frac{q_{e(\max)}C_e^b}{K^b+C_e^b}$  with  $q_{e(\max)}$ , *K* and *b* fitting parameters) than can describe sigmoidal complex behaviors, and, in several cases, is equivalent to the Langmuir adsorption model. 156

#### 157 2.4. Batch reactor experiments

Aqueous carbonation of portlandite in the presence of antibiotic was also monitored in real time 158 with Raman spectroscopy in order to identify the effect of antibiotics on the nucleation process of 159 calcite. Here, 2 g of synthetic portlandite was dispersed in 200 ml of an antibiotic solution (100 160 mg/L) placed inside of a hydrothermal reactor equipped with an in-situ Raman probe (RAMAN 161 162 RXN1, Kaiser Optical Systems). Then, 5-10 bar of  $CO_2$  was injected in the reactor and the system was monitored during 20-60 minutes at a rate of one acquisition every 0.25 or 1 min. This custom-163 build experimental setup has been used to investigate the nucleation, growth and transformation of 164 165 several mineral phases [23, 25-27]. For the Fenton reaction, two additional experiments were performed using 2 L beakers. Here, 1 L 166

of amoxicillin solution (130 mg/L, 0.6 ml of oxygenated water at pH=2.55) was stirred in the
 presence of 1 g of magnetite nanoparticles. Several fluid samples were withdrawn at different time
 intervals and the amoxicillin concentration was determined with UV-Vis spectroscopy.

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#### 171 2.5. Ex situ characterization of solids

Selected recovered solid samples were dried under air atmosphere at 60 °C for 48 h and stored in
plastic flasks for subsequent characterization by Field-Emission Scanning Electron Microscopy
(FESEM) and powder X-ray diffraction (PXRD).

175 XRD patterns were acquired using a Siemens D5000 diffractometer in Bragg-Brentano geometry,

- 176 equipped with a theta-theta goniometer with a rotating sample holder. Diffraction patterns were
- then collected using Cu k $\alpha_1$  ( $\lambda_{k\alpha_1}=1.5406$  Å) and Cu k $\alpha_2$  ( $\lambda_{k\alpha_2}=1.5444$  Å) radiations in the range

178  $2\theta = 10 - 70^{\circ}$ , with a step size of  $0.04^{\circ}$  and a counting time of six seconds per step. Coherent 179 average size of some samples was systematically refined by the quantitative Rietveld method on 180 XRD patterns using the BGMN software and its associated database [28].

181 Concerning the high-resolution microscopy imaging, the solid products were dispersed by 182 ultrasonic treatment in high purity water for five minutes. One droplet of the suspension was then 183 deposited directly on an aluminum support and observed without metal coating because calcite and 184 magnetite nanoparticles have enough conductivity. The powder was imaged using a Zeiss Ultra 55 185 FESEM with a maximum spatial resolution of ca. 1 nm at 15 kV.

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#### 187 **3. Results and discussion**

#### 188 *3.1. Removal of antibiotics by portlandite aqueous carbonation*

During a representative carbonation reaction of portlandite (Ca(OH)<sub>2</sub>) in a CO<sub>2</sub>-saturated solution, first the portlandite particles dissolve and release Ca<sup>2+</sup>. Immediately, amorphous calcium carbonate (ACC) particles precipitate, and transform into calcite (CaCO<sub>3</sub>) within a few seconds to minutes, as demonstrated by previous time-resolved Raman spectroscopy measurements [23]. In this way, the calcite growth process can incorporate, adsorb and/or enhance precipitation of ionic elements (Se, As, Cr, Fe, Mn, Sb, P and N) from polluted solutions, [19-20, 29-35] and also remove organic pollutants such as antibiotics as demonstrated in the present study.

Herein, we assessed the efficiency of the antibiotic removal via aqueous portlandite carbonation by comparing breakthrough curves obtained simultaneously from the inert and reactive tracer reactors. In our experimental setup, if the pollutant does not have any physiochemical affinity and/or reactivity with the dispersed solid particles, the breakthrough curves for inert and reactive tracers should overlap. However, if some interaction with the dispersed particles occurs, the -10-

breakthrough curve for the reactive tracer may display a significant retarding effect with respect to 201 202 the breakthrough curve of the inert tracer. In such case, a removal isotherm can be calculated by using Eq. 1. Figures 1 and 2 show breakthrough curves and removal isotherms for amoxicillin in 203 204 the presence of different starting amounts of portlandite. These curves reveal that a significant amount of amoxicillin is removed during aqueous carbonation of portlandite. This process is 205 directly related to initial available portlandite (1 or 2 g). The retarding of reactive tracer curve is 206 207 also proportional to the initial dose (see breakthrough curves in Figures 1 and 2). These results thus show that amoxicillin is sequestered during the carbonation process of portlandite, i.e. when calcite 208 209 is forming. A control experiment was performed where high purity calcite was used as potential 210 sequestration agent. In this case, breakthrough curves for inert and reactive tracers overlap (see Fig. SI-1), indicating negligible amoxicillin sorption/sequestration onto already formed calcite 211 particles. This result thus further confirms that amoxicillin is being retained from solution during 212 the initial stages of calcite formation. 213

The removal isotherms for amoxicillin, i.e. the removed amount as a function of equilibrium 214 concentration, are equivalent when 1 or 2 g of portlandite are used (Figures 1 and 2 on the right). 215 This result is consistent because the removed amount of amoxicillin was normalized with 216 portlandite mass and an equilibrium concentration in the percolating solution was assumed in these 217 218 flow-through experiments. Specifically, the fitted parameters from Hill's model show that the equilibrium constant K (equilibrium concentration, which represents also the half-removed amount 219 of pollutants), the maximum removed amount,  $q_{e(max)}$ , and Hill's coefficient, b, are equivalent for 220 both initial quantities of portlandite. K and  $q_{e(max)}$  are two fundamental parameters to calculate the 221 liquid-solid distribution coefficients ( $K_D = q_{e(max)}/K$ , given in [L/g]).  $K_D$  is widely used to 222 simulate the mass transfer at the solid-fluid interfaces in porous media [19]. Table 1 provides these 223 - 11 -

224 parameters for all fitted isotherms.

225 The removal of two other antibiotics (ceftriaxone and cefazolin) was also assessed. Figures 3 and 4 show the breakthrough curves and the removal isotherms for cefazolin and ceftriaxone, 226 respectively. These data show that both antibiotics are also efficiently removed from solution by 227 aqueous carbonation of portlandite. The removed amount versus equilibrium concentration follows 228 a similar trend for both antibiotics and the removal isotherms were again fitted using Hill's model 229 230 (Table 1). In summary, significant amounts of amoxicillin, ceftriaxone, and cefazoline can be removed by aqueous carbonation of portlandite. The plateaus in the isotherm curves of Figures 1, 231 2, 3, and 4 (on the right) show that the method is most efficient for amoxicillin (9.5 mg/g), followed 232 233 by cefazoline (4.3 mg/g) and ceftriaxone (2.7 mg/g). Erythromycin was also assessed, unfortunately, this antibiotic has low absorbance in UV vis spectroscopy at the investigated 234 235 concentration. For this reason, only qualitative results are commented in the following paragraphs. Noteworthy, the UV-Vis spectroscopy data reveal that the absorbance peak for amoxicillin, 236 237 cefazoline and ceftriaxone shifts to a higher wavelength in portlandite alkaline media. For example, amoxicillin absorbance shifts from 228 nm (typical in water) to 247 nm in a saturated portlandite 238 solution (Fig. SI-2). This is probably due to a strong complexation of amoxicillin with  $Ca^{2+}$  in an 239 alkaline solution because such peak shifts back to typical absorbance wavelength in water (i.e. 228 240 241 nm) when all portlandite was consumed in the system, i.e. when calcite precipitation had finished during a percolation experiment. The observed shifts also agree with a complexation study of 242 amoxicillin in Ca<sup>2+</sup> systems [36]. The UV-Vis time-resolved spectra during amoxicillin removal 243 244 by portlandite aqueous carbonation (Fig. 5) may be explained by a selective Ca complexation of this antibiotic under alkaline conditions, a process which could also contribute to antibiotic 245 removal. 246

To gain insight on the influence of antibiotic on the nucleation of calcite from aqueous carbonation of portlandite additional batch experiments were performed in real time using Raman spectroscopy. Results show that the presence of antibiotics does not change significantly the calcite nucleation mechanism. Amorphous calcium carbonate peaking at 1080 cm<sup>-1</sup> was detected as the only transient phase and its lifetime varied slightly with the different antibiotics in the range three to five minutes under our experimental conditions (Fig. 6).

253 FESEM images acquired on the recovered solid phase showed oriented aggregates of calcite crystals (resembling mesocrystals) for all antibiotics, except erythromycin where well-dispersed 254 255 nanoparticles of calcite were obtained (see Fig. SI-3). Average calcite particle sizes observed in 256 FESEM images agree with the average particle size extracted from powder XRD patterns. In particular, the average particle size for calcite varies when a given antibiotic is used, as revealed 257 258 by the full wide half maximum (FWHM) parameter. The position of the main reflection (104) varies also slightly, which is probably due to a minor incorporation of the antibiotic into the calcite 259 260 crystal lattice (see Fig. SI-4).

Our spectroscopic and textural data suggest that complexed antibiotic was mainly removed during the formation and transformation of amorphous calcium carbonate (ACC) into calcite. We interpret that the organic material adhered onto calcite nanoparticles, inducing the formation of mesocrystals, a process that was previously observed during calcite formation via aqueous carbonation of portlandite in presence of common domestic drinks [37].

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#### 267 *3.2. Removal of amoxicillin by Fenton reaction*

Advanced oxidation of organic pollutants via the so-called Fenton process has been investigated and implemented in modern wastewater plant treatment [38]. For this reason, we investigate here

270 a modified Fenton reaction using nanosized magnetite as ferrous source for amoxicillin removal, 271 in order to compare it with the aqueous carbonation of portlandite method. A typical Fenton oxidation process involves complex redox and decomposition reactions between several reactants 272 (ferrous iron, oxygenated water and antibiotic) at low pH in the range 2.5-3.5. In our experiments, 273 we varied the concentration of oxygenated water, magnetite particle size and pH adjustment. The 274 antibiotic removal amount was exclusively obtained when the pH was pre-adjusted to 2.6 and when 275 276 260 mg/L of oxygenated water and magnetite nanoparticles were used. In this case, the amoxicillin was partially oxidized by Fenton reaction, as revealed by the breakthrough curves for inert and 277 278 reactive tracers (Fig. 7). Herein, the ferrous iron was provided from surface magnetite dissolution 279 enhanced at low pH in the presence of oxygenated water. Then the oxidation of amoxicillin took place at the surface of the magnetite nanoparticles, including two main reactions taking place at 280 281 the nanoparticle-solution interface:

$$282 \quad Fe^{2+} + H_2O_2 \Longrightarrow Fe^{3+} + \bullet OH + OH^-$$
(2)

283 Antibiotic + 
$$\bullet$$
OH  $\Rightarrow$  CO<sub>2</sub> + H<sub>2</sub>O + inorganic-matter (3)

The oxidation and/or degradation process of antibiotics can imply various intermediate steps, as 284 determined for amoxicillin in aquatic environment [39]. In our case, a simpler approach was used 285 286 by measuring the residual amoxicillin in water during flow-through experiments at different time intervals using UV-Vis spectroscopy. The breakthrough curve for the reactive tracer shown in 287 Figure 7 reveals a significant retarding with respect to the inert tracer after seven hours of 288 percolation and the reaction is still active because the concentration in the outlet solution has not 289 290 reached the concentration of the inlet solution. This indicates that the oxidation of amoxicillin is a 291 relatively slow process.

292 Importantly, the removal isotherm shown in Fig. 7 (on the right) did not reach the maximum 293 amount of removed amoxicillin calculated by Hill's model. This model estimates a maximum removal amount of about 76 mg/g (see Table 1 and projection curve on Fig. SI-6). In order to 294 validate this calculation, we performed several batch reactor experiments (volume 1 L). The 295 obtained data showed that 33 mg of amoxicillin per g of magnetite nanoparticles were removed 296 after 7-24h (Fig. SI-7). This result agrees well with the flow-through experiments and both 297 298 experimental configurations indicate that the Fenton reaction was probably passivated by iron oxidation at the magnetite-solution interfaces, but such reactions remained active during several 299 300 hours in flow-through and batch reactors as demonstrated in the present study. In practice, as 301 expected the interfacial-magnetite Fenton reaction is also an efficient method to remove amoxicillin from water. But, this reaction is not active when the pH is not adjusted to 2.6; here, the 302 303 amoxicillin oxidation is not active and/or negligible as revealed by an overlapping of breakthrough curves for inert and reactive tracers (Fig. SI-5). A similar inactivation of the Fenton reaction was 304 observed at lower concentrations of oxygenated water and when microparticles of magnetite were 305 used instead of nanoparticles. 306

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#### **308 4. Conclusion**

Amoxicillin can be successfully removed from water using a flow-through setup implementing aqueous carbonation of portlandite or an interfacial-magnetite Fenton reaction. Both methods can efficiently remove these antibiotics from water as demonstrated with breakthrough curves and their respective removal isotherms. The interfacial-magnetite Fenton reaction offers a better removal capacity for amoxicillin with respect to aqueous carbonation of portlandite. Importantly, the solidliquid separation could be facilitated because the reacting magnetite particles preserve their

315	magnetic potential, and this Fenton reaction can be used to remove organic pollutants from water
316	at an industrial scale. We also assessed the removal capacity of the carbonation method for two
317	other antibiotics, ceftriaxone and cefazoline. In overall, aqueous carbonation of portlandite offers
318	a more promising and easier operating method to remove antibiotics from water because it can be
319	implemented without significant modification of existing water treatment plants, for example, by
320	using coagulation units that are already present in these plants. In our method, the treated water is
321	neutralized with $CO_2$ during aqueous carbonation of portlandite and the pH at the outlet flow is
322	close to 7. This water could be directly discharged into nature, reused, or undergo additional
323	treatment. In addition, this method can also be used to efficiently remove ionic pollutants such as
324	heavy metals and metalloids (e.g. As, Se and Fe). Moreover, the generated solid product, about
325	1.35 kg of high purity calcite per m <sup>3</sup> of treated water, can be re-used in a variety of industrial
326	applications such as additive and mineral filler (e.g. plastics, paper, paintings, etc.).
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344	Appendix A. Supplementary data
345	The supplementary material contains seven figures, provided in the online version, at the following
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- Table 1. Summary of equilibrium parameters from Hill's model used to fit the data of the removal
- of antibiotics from water by portlandite aqueous carbonation and by nanomagnetite-interfacial

Fenton reaction. Experimental isotherms were determined from breakthrough curves (Eq. 1).

		Parameters used to fit Hill's model				
Antibiotic	Mineral	K mg/L	q <sub>e(max)</sub> mg/g	b	$K_D = q_{e(max)}/K$ L/g	Process
Amoxicillin	Portlandite (1g)	30.62±0.22	9.48±0.03	5.84±0.27	0.30	Aqueous carbonation
Amoxicillin	Portlandite (2g)	29.74±0.36	8.35±0.09	9.32±1.35	0.28	Aqueous carbonation
Cefazolin	Portlandite (1g)	56.10±0.73	4.27±0.04	10.11±1.24	0.08	Aqueous carbonation
Ceftriaxone	Portlandite (1g)	66.59±0.49	2.69±0.02	16.43±1.81	0.04	Aqueous carbonation
Amoxicillin	Magnetite Nanoparticles (1g)	130.75±22.02	76.52±*	9.30±1.48	0.58	Fenton reaction

K: equilibrium concentration producing half-removed amount,  $q_{e(max)}$ : maximum removed amount, b: Hill's coefficient,

 $K_D$ : liquid-solid distribution coefficient, \*:very high error 











is strongly complexed with calcium during carbonation process of portlandite (see reactive tracer reactor at right) because amoxicillin UV-Vis absorbance backs to typical absorbance when portlandite was completely consumed in the system.

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Figure 6. Time-lapse Raman spectra for calcite nucleation in presence of four different antibiotics, and reference without antibiotic. In all cases, amorphous calcium carbonate (ACC, blue halo on the figures) formed prior to calcite nucleation and was detected after the first minute of CO<sub>2</sub> injection. Its lifetime was similar and close to three minutes for all experiments, except in the presence of erythromycin where it was five minutes. 







Figure 7. Left: Experimental breakthrough curves for inert tracer (reactor without magnetite) and 583 reactive tracer (reactor with magnetite (1g)) during the removal of amoxicillin by aqueous 584 magnetite-interfacial Fenton reaction (standard deviation<5% after equilibration of inert tracer 585 curve). Right: Amoxicillin removal isotherm from breakthrough curves determined by Eq. 1 and 586 data fitted with Hill's model (error of fitted parameters provided in Table 1). 587