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1	Peroxydisulfate activation by CuO pellets in a fixed-bed column,
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20 Abstract

21 A fixed-bed column packed with copper oxide pellets (FBC-CuO) combined with 22 peroxydisulfate (PDS) as a primary oxidant was assessed as an option for 23 simultaneously wastewater decontamination (antibiotics) and disinfection (bacteria, 24 viruses, and protozoa). Preliminary to these experiments, phenol was used as the target 25 molecule to investigate the working mode of FBC-CuO under various operating 26 conditions, such as varying flow rates, initial persulfate and phenol concentrations. 27 Then, the removal of a mix of five representative antibiotics (amoxicillin (AMX), cefalexin (CFX), ofloxacin (OFL), sulfamethoxazole (SMX), and clarithromycin 28 29 (CLA)) in secondary treated urban wastewater (STWW) was evaluated. AMX, CFX, 30 and OFL were effectively removed by simply flowing through the FBC-CuO, and the 31 addition of PDS (500 µM) systematically enhanced the degradation of all targeted 32 antibiotics, which is also the necessary condition for the removal of SMX and CLA. 33 Urban wastewater disinfection was evaluated by monitoring targeted pathogens originally in the STWW. A significant reduction of E. coli, Enterococcus, F-specific 34 RNA bacteriophages was observed after the treatment by FBC-CuO with 500 µM PDS. 35 X-ray diffraction measurement and scanning electron microscopy performed on CuO 36 37 pellets before and after treatment confirmed that the structure of the catalyst was 38 preserved without any phase segregation. Finally, quantification of Cu(II) at the outlet 39 of FBC-CuO indicate a non-negligible but limited released. All these results underline 40 the potential of the FBC-CuO combined with PDS at the field scale for the degradation 41 of micropollutants and inactivation of pathogens in wastewater.

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Keywords: Fixed-bed column; copper oxide pellet; operating parameters; antibiotics;
disinfection; secondary treated wastewater

46 **1. Introduction**

47 Conventional urban wastewater treatment plants are poorly effective to 48 comprehensively remove most organic micropollutants, pathogens, as well as antibiotic 49 resistance genes (Ternes et al. 2017; Rizzo et al. 2020). The occurrence and the large 50 discharging amounts of these contaminants in municipal wastewater is a concern due 51 to its potential ecotoxicological and hazardous effects on receiving nature waters or 52 reclaimed wastewater reuse (Wang et al. 2020). Therefore, effective additional treatment steps for micropollutants degradation, pathogens inactivation, as well as 53 54 antibiotic resistance reduction are required.

Advanced oxidation processes (AOPs) employing hydrogen peroxide and persulfate 55 56 have been seen as a promising technology for water decontamination and disinfection simultaneously, which rely on radical and non-radical reactive species produced by 57 activating oxidants, such as sulfate radicals (SO_4^-) , singlet oxygen $(^1O_2)$, and high 58 59 valent metal ions (Waclawek et al. 2017; Lee et al. 2020; Rizzo et al. 2020; Chen et al. 60 2021). Oxidants activation can be achieved by an input of energy (UV, heat), electrolysis, transition metal ions, metal oxides, carbon materials, etc. (Wang and Wang 61 62 2018; Brienza et al. 2019; Lee et al. 2020). However, the high cost of the required extra energy, the recycling difficulty of metal ions limit their application. In an attempt to 63 64 overcome these disadvantages, heterogeneous Fenton-like processes using different recyclable solid catalysts, such as iron oxides (Yan et al.2011; Obra et al. 2020; Luo et 65 al. 2021) or copper oxide (CuO) (Du et al 2017; Ding et al. 2022), have been developed 66 67 recently, and have shown high decontamination and disinfection capacity.

Among them, the CuO activated peroxydisulfate (PDS) system is an attractive option for potential application in organic matters enriched urban wastewater treatment (Zhang et al. 2014; Du et al 2017; Li et al. 2021; Ding et al. 2022; Li et al. 2022) due to the mild non-radical activation pathways combined with the highly selective reactive species production. The mechanisms of organic compounds degradation and pathogens 73 inactivation by the CuO/PDS system have been investigated in details by previous 74 studies (Liang et al. 2013; Zhang et al. 2014; Du et al 2017; Cho et al. 2020; Zhou et al. 75 2020). Specifically, in the recent studies of our research group carried out in batch 76 operating mode, in beaker, with micro-sized particles (Li et al. 2021; Li et al. 2022), 77 the CuO/PDS system has been confirmed as effective for degradation of organic pollutants (i.e., phenol and several antibiotics), inactivation of pathogens and antibiotic 78 79 resistant-bacteria and resistance genes. Cupryl ion (Cu(III)) was highlighted as the 80 predominant reactive species, which could selectively oxidize the electron-rich 81 phenolic amino acids, antibiotics (i.e., cefalexin, ciprofloxacin, sulfamethoxazole, and 82 clarithromycin), as well as guanine and L-tyrosine, thus causing damages to the DNA and protein of bacteria and viruses. 83

84 With a mid-term perspective of large scale applications, the study of CuO/PDS systems 85 carried out in fixed bed column operating in open and continuous flow is a relevant step. 86 Although already tested in the case of micro-sized particles for 2,4-dichlorophenol 87 degradation (Zhang et al. 2014) and nanoparticles supported on alumina granules for 88 virus removal evaluation (Mazurkow et al. 2020), this option has received very few 89 attentions in the literature. Thus, even if processes based on fixed-bed column are very 90 well known in chemical engineering and well identified to provide efficient components 91 separation by catalytic treatment or chemical reactions (Levenspiel 1972, Crittenden et 92 al. 2012; Andrigo et al. 1999), there are still a lot of unknowns about the working mode 93 and performances of a CuO/PDS advanced oxidative system operating according a 94 packed bed principle.

The objectives of this paper is to provide first experimental trials of PDS activation for antibiotics degradation and urban wastewater disinfection with a fixed-fed column filled with millimetric CuO pellets (FBC-CuO). Prior to these tests, an extended experimental study was carried out in the case of a very basic effluent to be treated, that consisted of phenol in distilled water with Tris buffer (DW). Data were collected for different operating parameters, such as the inflow PDS concentration or flow rate, to
 provide a clear and argued qualitative description of the operating mode of this process.

102 The most commonly used and frequently detected in the environment family of 103 antibiotics in the world are the β -lactam antibiotics, including penicillins and 104 cephalosporins. Amoxicillin (AMX) and cefalexin (CFX) are belongings to the 105 aminopenicillin and cephalosporins family, which have been detected in raw sewage, 106 effluents of sewage treatment plants, and even surface waters (Hirte et al. 2016; Qian 107 et alk.2018). In addition to β -lactam antibiotics, sulfonamide, macrolide, as well as 108 fluoroquinolone antibiotics are the most prominent classes of antimicrobial agents, with 109 widespread usage in both human and veterinary medicines, which occurs ubiquitously in aquatic systems that are influenced by anthropogenic activities (Schönfeld et al. 1986; 110 111 Gmurek et al. 2015; Poirier-Larabie et al. 2016; Senta et al. 2017). The evaluation of 112 the antibiotics removal efficiency in DW and secondary treated waste water (STWW) 113 was performed by using a mixture i.e. amoxicillin (AMX), cefalexin (CFX), ofloxacin 114(OFL), sulfamethoxazole (SMX), selected to cover a the broad spectrum of antibiotics 115families. The evaluation of STWW disinfection performance is assessed by using 116 Escherichia coli (E. coli), Enterococcus, F-specific RNA coliphages, and spores of 117 sulfite-reducing bacteria as pathogenic indicators. Catalyst stability evaluation by 118 analyzing the Cu(II) leaching and comparing the morphology and crystallinity of CuO 119 pellet before and after treatment complement the characterizations of the FBC-CuO 120 process.

121 **2. Experimental section**

122 **2.1 Chemicals**

123 CuO pellet (> 99.9%) was purchased from Merck (Germany). Phenol, amoxicillin

124 (AMX), cephalexin (CFX, >99%), clarithromycin (CLA, >99.9%), ofloxacin (OFL, >

125 99.9%), sulfamethoxazole (SMX, > 99.9%), potassium peroxydisulfate (K₂S₂O₈, >

126 99.9%), sodium thiosulfate (NaS₂O₃), and EDTA were purchased from Sigma-Aldrich

(Saint Quentin Fallavier, France). Potassium iodide (KI), potassium periodate (KIO₄),
and tris(hydroxymethyl)aminomethane (Tris) were purchased from Merck KGaA
(Germany). Acetonitrile (HPLC grade), methanol (MeOH, HPLC grade), and sodium
chloride (NaCl) were purchased from Carlo Erba reagents (France). All the reagents
used were of analytical grade and were used as received. Milli-Q water from a DirectQ® system (Millipore) was used for the stock solution preparation and the HPLC
analyses.

134 **2.2 CuO pellets**

The CuO pellets (0.7-2 mm) morphology was analyzed using JEOL 6490 scanning electron microscope (SEM). X-ray diffractometry (XRD) was performed using a Bruker D8 Advance in Bragg-Brentano geometry with a Cu source. Diffraction signal has been acquired through theta/2theta scans from 10 to 80° with 0.02° step, with an acquisition time of 1s/step.

140 2.3 Fixed-bed column set up

The FBC-CuO column consisted of a cylinder stainless steel cylinder (18 mm internal 141 diameter (I.D.) \times 200 mm height) filled with 140 g of CuO pellets. The use of 142 143 millimetric CuO pellets allowed to respect the requirement of limiting the pressure drop 144 inside a column (Metha and Hawley 1969) and preventing potential clogging problems. 145Two metal grids with a mesh smaller than the size of the CuO pellets were positioned 146 at the inlet and the outlet of the column. FBC-CuO consists of a volume occupied by 147 the solid CuO pellets (22 mL) and an empty bed volume (EBV, 29 mL) corresponding 148 to an experimental porosity equal to 0.55. As shown in Fig. S1, the FBC-CuO was 149 vertically oriented and silicone tubes were connected at both ends. The inlet at the 150bottom of the column was driven by a peristaltic pump (lab 2015, Shenchen, China) to 151control flow rates, and the outlet was at the top of the column. Three micro-valves were 152evenly located on the column evenly 5 cm for local sampling and accessed the internal

concentration profiles of the different components. All experiments were operated inupflow mode at a controlled flow rate.

155 **2.4 Experimental procedures**

156 2.4.1 Phenol degradation with FBC-CuO/PDS process

157 To have a thorough understanding of the working mode, phenol was selected as the 158probe compound. Tris buffer (20 mM) was used as the water matrix to maintain the 159 neutral pH of the solution for all the experiments with phenol. As no adsorption or 160 degradation of phenol by CuO alone were observed (Li et al. 2021), it was decided to 161 start the experiments with a column filled with the phenol solution. Pure phenol solution 162 (5 mg/L) flowed from a tank into the column with a 3 mL/min flow rate until the outlet 163 concentration equal the inlet concentration. A uniform concentration of phenol inside 164 the column represented the initial conditions of the degradation experiments. 165 Experiments were systematically triggered by the addition of PDS to the phenol 166 solution and a flow into the column according to the selected flow rate. From this 167 starting point, the solution flow rate and the inlet phenol and PDS concentrations kept 168 unchanged. Aliquots of treated water samples were collected at the predetermined time 169 from the outlet and three valves. Samples were stored at 4 °C before analysis. The 170 working mode of the phenol removal was expected to happen in a first phase in dynamic 171regime and followed by a second phase in permanent regime.

172 2.4.2 Antibiotics degradation with FBC-CuO and FBC-CuO/PDS processes

To evaluate the degradation performance of antibiotic micropollutants on the FBC-CuO column, 250 μg/L of AMX, CFX, OFX, SMX, and CLA, which have been commonly detected in urban wastewater, were spiked to DW and STWW from an activated sludge wastewater treatment plant, respectively. The physio-chemical properties of STWW are listed in Table S1. STWW was firstly filtered through a 200 μm sieve to remove the largest suspended solids and prevent the clogging problem.

Differently with phenol, the interaction between Cu(II) with some specific antibiotics was previously reported (Lapshin and Alekseev 2009; Chen et al. 2019). Thus, the starting point of the antibiotic degradation experiments was corresponding to the FBC-CuO filled with pure water. Firstly, the antibiotics mixture solution flowed through the column without PDS, then a constant inlet concentration of PDS was added in the inlet solution. Aliquots of treated water samples were collected at the predetermined time from the column outlet, and stored at 4 °C before analysis.

186 2.4.3 Pathogens inactivation with FBC-CuO and FBC-CuO/PDS processes

187 STWW was collected from the same activated sludge wastewater treatment plant and was also filtered through a 200 µm sieve before the disinfection experiment. To 188 189 evaluate the disinfection performances and to comply with the EU Regulation 2020/741 190 of the European Parliament on minimum requirements for water reuse, E. coli, 191 Enterococcus, F-specific RNA bacteriophages, and spores of sulfite-reducing bacteria 192 were selected as the indicator of Gram-negative, Gram-positive bacteria, virus, and 193 protozoa, respectively. The pathogenic indicators originally presented in wastewater 194 were targeted to monitor.

195 It was checked that at ambient temperature PDS alone as no effect on the different indicators (Li et al. 2022). At the opposite, CuO alone, may interact and provide non-196 197 negligible disinfection effects (Ren et al. 2009; Suleiman et al. 2015; Li et al. 2022), 198 especially when implemented in the form of nanoparticles. For this reason, disinfection 199 experiments were operated as in the case of the experiments dedicated to antibiotic 200 degradation. A first step corresponding to the flowing of the effluent through the FBC-201 CuO system without PDS. A second step corresponding to the flowing of the effluent 202 at the same flow rate with a constant concentration of PDS at the inlet of the column.

The column was design to operate with flow rates of few mL/min to provide consistent residence times. Measurement of the four targeted pathogens needed to collect one liter of each sample. As a consequence, it was not possible to investigate the pathogens 206 inactivation process in dynamic regime due to the long sampling period, and the 207 sampling was carried out in the both cases (with and without PDS) when the permanent 208 regime was reached after at least 2 hours of operating.

209 To ensure the stable viability of pathogens, the effluents in the sterile water tanks at the 210 inlet and outlet of the column were surrounded by ice pads. Samples were stored at 4 °C

and pathogens analysis was conducted less than 24 h after sample collection. 211

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213 2.5 Analytical methods

214 2.5.1 Quantification of phenol and PDS

215 Phenol concentrations were quantified by LC with a diode-array detector at $\lambda = 280$ nm 216 using an Agilent ZORBAX Eclipse XDB C8 column (150 × 3 mm i.d., 3.5 µm particle 217 size). The separation was performed using an isocratic mode of elution with a mobile 218 phase composed of 0.1% formic acid in Milli-Q water and acetonitrile at a volume ratio 219 of 50/50. The flow rate was set at 0.5 mL/min. The injection volume of each sample was 10 µL. 220

221 PDS was determined by using a UV-Vis spectrophotometer (Shimadzu, Japan). Briefly,

the method already reported (Li et al. 2021) consisted in analyzing adsorption spectra 223 of mixed solutions of 1 mL sample, 1 mL 60 mM NaHCO₃, and 1 mL 600 mM KI in a

224 quartz cuvette at $\lambda = 352$ nm.

225 2.5.2 Quantification and transformation products analysis of antibiotics

226 Quantification of targeted antibiotics were analyzed by LC-HRMS composed of a 227 Dionex Ultimate 3000 liquid chromatograph equipped with an electrospray source 228 operated in the positive ionization mode and a Exactive Orbitrap mass spectrometer 229 (Thermo Fisher Scientific, Les Ulis, France) operated in full scan MS (mass range m/z 230 50-900) and using an Agilent ZORBAX Eclipse XDB C18 plus column (150×2.1 mm 231 i.d., 3.5 µm particle size). LC gradient of Milli-Q water with 1% acetonitrile and 0.1%

formic acid (solvent A) and acetonitrile with 1% Milli-Q water and 0.1% formic acid (solvent B) was as follow: 0-5 min, 95% A; 15-20 min, 5% A; 21-30 min, 95% A. The flow rate was 0.15 mL/min. The energy collisional dissociation was set to 20 eV and a drying gas temperature of 300 °C was used. The injection volume of each sample was 10 μ L.

To gain insights into the targeted antibiotic degradation mechanisms of FBC-CuO alone, and FBC-CuO in presence of PDS, transformation products (TPs) of AMX, CFX, OFL, SMX, CLA were identified following a suspect screening workflow in LC-HRMS. The databases were made up of a list of possible TPs with their molecular formula and exact mass collected from the literature. The list of possible TPs of CFX, SMX, CLA were reported in the supplementary information in our previous study (Li et al. 2021). Possible TPs of AMX and OFL were listed in Table S2-S3.

244 2.5.3 Enumeration of pathogens

The NF EN ISO 9308-3 and NF EN ISO 7899-1 standard protocols were used to 245 246 enumerate E. Coli and Enterococcus respectively. These methods are based on the 247 culture of the bacteria in a liquid medium and the determination of the most probable 248 number (MPN) according to the level of dilution. F-specific RNA bacteriophages were 249 measured according to the ISO 10705-1 method. This method allows for a count on the 250agar medium of plaque-forming unit (PFU), corresponding to the number of viruses. 251 The NF EN 26461-2 standard protocol was used to enumerate the colony-forming unit 252 (CFU) of spores of sulfite-reducing bacteria after filtration and cultivation on a specific 253 agar solid medium.

254 2.5.4 Cu(II) analysis

255 Cu(II) leached from CuO pellet was analyzed by inductively coupled plasma - optical 256 emission spectrometry (ICP-OES) using an iCap Duo 7400 spectrometer (Thermo 257 Fischer Scientific, Les Ulis, France) using the axial mode of detection at wavelength λ 258 = 324.754 nm.

259 **3. Results and discussion**

260 **3.1 Working mode of the CuO pellet fixed-bed column**

261 As detailed in the section 2.4.1, before each degradation experiment, the column was 262 charged with a pure phenol solution at a given concentration. Fig. 1a presents the 263 breakthrough curve of the phenol at the outlet of the column in the case of a volume 264 flow rate equal to 3 mL/min and an inlet concentration of phenol (C_{ph} i) equal to 5 mg/L. 265 The Reynolds number (Re) under flowing conditions was much smaller than 1, indicating a highly laminar flow regime in the column. The axial diffusion coefficient 266 is estimated to be in the range of 2×10^{-6} m²s⁻¹ with the popular and simplified Chun and 267 268 Wen (1968) empirical equation (Table S4) adapted to flowing conditions with Re < 1. 269 As expected, and in agreement with the low value of the Peclet number (around 0.2), 270 the shape of the breakthrough curve was characteristic of a plug-flow with an important 271 axial dispersion resulting in an "S-curve". Finally, the theoretical phenol quantity 272 calculated taking into account the EBV and the minor dead volumes at the inlet and the 273 outlet of the column, was equal to the actual phenol quantity calculated from the 274 breakthrough curve (around 0.14 mg), which further confirmed that there was no 275detectable adsorption of phenol at the surface of the CuO pellet and no scalable 276 persistent interaction between this molecule and the CuO.

277 For the record, the initial time (t = 0) in Fig. 1b corresponds to a column with a uniform 278 inlet and outlet phenol concentration ($C_{ph_i} = C_{ph_o} = 5 \text{ mg/L}$) and without any trace of 279 PDS but operating, from this moment with a volume flow of 3 mL/min, and inlet PDS 280 (C_{PDS i}) and phenol concentrations equal to 500 µM and 5 mg/L respectively. As 281 expected, the column operated in two different regimes. The first dynamic regime 282 corresponded to the establishment of the PDS and phenol concentration profiles in the 283 fixed packed bed. During this phase, the concentrations of both species inside the 284 column were the result of the coupling between the convective mass transport, mass 285 diffusion of both species, kinetic of phenol removal, and kinetic of PDS consumption.

286 The breakthrough time of the PDS (Fig. 1b) was consistent with the one obtained in the 287 case of phenol during the preliminary charge, and gave the limit between the dynamic 288 and the permanent regime. It took at least 40 to 50 min for a completed establishment 289 of the permanent regime, and then the concentrations of both species remained constant 290 at the outlet. Their absolute values depended on the operating parameters of the column 291 i.e., the volume flow rate and the inlet concentrations of phenol and PDS. For the 292 selected conditions, phenol was almost complete removed but PDS was not fully 293 consumed. Around 20% of the PDS at the inlet of the column remained at the outlet. 294 After 60 min, the local concentrations of phenol and PDS were very stable at any 295 position inside the column during the entire measurement period of several hours (Fig. 296 1c and d), which well confirmed the fully steady-state operation of the process. The 297 profiles also clearly indicated that, for these particular operating conditions, the inlet 298 concentration of the PDS was in excess. PDS remained at the outlet of the column while 299 only half of the column was necessary to provide complete removal of the inlet phenol 300 flux (Fig. 1c).

301

302 The performance of the FBC-CuO with 5 mg/L influent phenol and 3 mL/min flow rate 303 was tested at varying influent PDS concentrations. Whatever were the working 304 conditions, the two regimes were checked with a period necessary for the establishment 305 of the quasi-static regime almost independent of the PDS inlet concentration (Fig. 2a 306 and c). Obviously, PDS dosage was a major factor that determined the column performances. As expected, higher influent PDS concentration promoted the oxidative 307 308 mechanisms and led to higher phenol removal efficiency and treatment capacity (Table 309 1). A twofold increase in the treatment capacity was observed when PDS concentration 310 varying from 125 μ M to 500 μ M. With 125 μ M at the inlet, there was no more PDS in 311 the solution at an axial position between 5 and 10 cm (Fig. 2d). From this position, the 312 concentration of the phenol remained constant (Fig. 2b). In the case of a too much low 313 inlet PDS concentration, all the oxidant was consumed in the front part of the column,

314 leading to an unused bed length were no degradation of the pollutant happened. On the 315 contrary, a too high inlet PDS concentration was inefficient and counterproductive. No 316 improvement of the treatment capacity was detected when PDS inlet concentration was 317 increased from 500 μ M to 1000 μ M (Table 1) while a useless release of PDS at the 318 outlet happened (Fig. 2c). As in the previous case but for a different reason, a too high dosage of PDS (1000 µM) also led to an unused bed length. In the first part of the 319 320 column, the high removal kinetic of phenol linked to the high level of PDS 321 concentration led to complete removal of the phenol between 5 and 10 cm (Fig. 2b). 322 For these particular conditions, a mass flow of 3 mL/min and an inlet concentration of 323 phenol of 5 mg/L, an inlet concentration of PDS between 250 and 500 µM would have 324 probably been the optimal value to achieve no PDS release at the outlet with a total 325 phenol removal thanks to an optimal use of the length of the column.

326

Table 1. Removal efficiency and treatment capacity of phenol by FBC-CuO/PDS
 system with varying influent PDS concentration.

Flow rate (mL/min)	C _{ph_i} (mg/L)	C _{PDS_i} (µM)	Removal efficiency (%)	Treatment capacity of phenol (µg/min)
		0	0	0
		125	46	7.41
3	5	250	81	12.36
		500	95	14.14
		1000	97	14.55

329

Even if only specific operating conditions were provided for a particular column design, this qualitative analysis clearly demonstrated that the control of the FBC-CuO process can easily be achieved by controlling and regulating the inlet oxidant concentration. This was further confirmed by the results conducted within the objective of studying the effects of the phenol inlet concentration, the volume flow, and presented as supplementary material (Fig. S2-S3).

336 **3.2 Degradation of antibiotics**

In the case of trials carried out in distilled water (Fig. 3a and 3b), as detailed in the 337 section devoted to the experimental procedure, in a first step, a mixture of AMX 338 339 (penicillin), CFX (cephalosporin), OFL (quinolone), SMX (sulfonamide), and CLA 340 (macrolide) in DW flowed through FBC-CuO at a flow rate of 1.5 mL/min. Different trends were noticed (Fig. 3a). In this case, corresponding to a more complex mixture 341 342 with probably competitive phenomena between the surface of CuO and some of the pharmaceutical compounds, the breakthrough times of each species were not uniform. 343 However, only a few tens of minutes separated the breakthrough times of SMX and 344 345 CLA, the two species with a fully breakthrough at the outlet of the column which happened around 1 h. This order of magnitude was in agreement with a breakthrough 346 347 derived from the resident time (35 min in the working conditions) combined with significant diffusional transport phenomena. CFX and OFX corresponded to an 348 intermediate behavior. Breakthrough happened but saturation of the column was never 349 350 reached. The outlet concentrations of both species kept lower than the inlet 351 concentrations, even after a very long operating period (18 h) and a permanent regime 352 definitively established as clearly indicated by the concentration profiles of the species. 353 Finally, whatever was the operating period, AMX was always undetectable at the outlet 354 of FBC-CuO. AMX, CFX, and OFL were completely or partially removed by FBC-355 CuO alone (Table 2).

356 Hydrolysis of β -lactam antibiotic family can be a significant degradation pathway in the environment, but it usually takes 5.3-27 days at pH 7 and 25°C (Mitchell et al. 2014). 357 358 It could not be the main degradation pathway in this study. Adsorption mechanism was 359 excluded because of the very low specific surface area of CuO (Li et al. 2021). Another 360 possible mechanism may be the complexation of Cu(II) with β -lactam antibiotics 361 (AMX and CFX) and fluoroquinolones (OFL). AMX and CFX contain the carboxylic, 362 amide, and amino groups, which resemble dipeptides in acid-base and ligand properties, 363 and exist as anions at neutral pH, then subsequently interact with Cu(II) (Lapshin et al.

364 2009; Lipunova et al. 2009; Chen et al. 2019). Transformation products of AMX, CFX, 365 and OFL in FBC-CuO were identified following a suspect screening workflow in LC-366 HRMS. For this purpose, a database was made up of a list of possible TPs with their 367 molecular formula, exact mass, and structure (see Table S1 and S2, and SI of previously 368 work by our group (Li et al. 2021)). This list was established from a literature search of TPs. TPs with intensities lower than 1×10^4 cps, signal to noise ratios lower than 10, 369 isotopic ratio higher than 10%, and mass accuracy errors higher than 5 ppm were 370 371 discarded. The identified TPs of CFX, AMX, and OFL were shown from Fig. S4, S5, 372 S6 representatively. The transformation pathways of AMX, CFX, and OFL in FBC-373 CuO were tentatively elucidated (Fig. S7). The formation of TPs most likely through a 374 one electron transfer from the antibiotic to the metal in the complex, demonstrated the 375 evidence of the degradation of AMX, CFX and OFL by FBC-CuO alone. Actually, a detail study of transformation mechanims were outside the scope of this work. However, 376 377 the compounds which underwent removal (AMX, CFX and OFX) were those which form a complex with copper. That's why we assumed that copper played a role in their 378 379 elimination may be through one electron oxidation processes or by accelerating the 380 hydrolysis of the lactam ring. But these mechanisms were not demonstrated in this work 381 and will deserve more research. In case of AMX, the direct reaction between AMX and 382 singlet oxygen could not be discarded as previously reported (Zhao et al., 2013). However, the formation of singlet oxygen was not demonstrated in FBC-CuO system 383 384 and could be only anticipated in presence of PDS.

After 18 h of operation, the column was in permanent regime, 500 μ M PDS was added to the inlet water tank. As shown in Fig. 3b, the addition of PDS systematically and significantly enhanced the degradation of the antibiotics. The residual outlet concentration of CFX and OFL were rapidly removed. The presence of PDS was also the necessary condition for a partial but significant, removal of SMX and CLA. CFX and OFL were completely degraded after 30-40 min. 51 ± 2% of SMX and 34 ± 1% of 391 CLA were removed in the tested operating conditions when the quasi-permanent regime392 was reached.

393 In addition to DW, the removal efficiency of target antibiotics mixture in the actual 394 wastewater operating under the same conditions was also evaluated, as shown in Fig. 395 4c and 4d. The degradation tendency of target antibiotics in DW and STWW was the 396 same, however, the removal efficiency of targeted antibiotics decreased under the 397 influence of various competitive components in the STWW (Fig. 3 and Table 2). For 398 the first stage of FBC-CuO, the dissolved organic matter and anions (e.g. sulfate anions) 399 in STWW could interact with Cu(II) or adsorbed on the CuO, resulting in less available 400 activated sites on the CuO surface, and limited Cu(II) complexation with targeted antibiotics (Fig. 3a and c). For the second stage, less PDS could interact with CuO, 401 402 resulting in less PDS consumption (Fig. S8), less reactive species production, and lower 403 degradation efficiency for all targeted antibiotics (Fig. 3b and d). According to our 404 previous work dealing with mechanisms of activation of persulfate in CuO/PDS system (Li et al, 2021), PDS activation is launched by the interaction between the positively 405 406 charged CuO and the negatively charged PDS. In this first work, it was shown that 407 anions such as sulfate anions and DOM can preclude or limit the interaction between 408 CuO/PDS resulting in a decrease in efficiency. Sulfate anions and negatively charge 409 DOM most likely interacted with positively charged CuO competing with antibiotics 410 and/or PDS for interaction at CuO surface.

411

DW **STWW** RE FBC-CuO FBC-CuO/PDS FBC-CuO FBC-CuO/PDS AMX (%) 100 100 59 ± 3 100 70 ± 2 100 25 ± 1 52 ± 2 CFX (%) OFX (%) 34 ± 1 100 31 ± 1 90 ± 2 0 0 20 ± 1 SMX (%) 51 ± 2 CLA (%) 0 34 ± 1 0 20 ± 1

Table 2. Removal efficiency (RE) of selected antibiotics by FBC-CuO alone and FBC CuO/PDS in DW and STWW.

414 **3.3 Pathogens inactivation**

415 In a first step, the STWW was flowed through the FBC-CuO at a flow rate equal to 3 416 mL/min. After 2 h of operation, the working mode of FBC-CuO was expected to reach 417 the permanent regime. From this moment, the sampling at the outlet of the column started to collect the necessary 1 L effluent for pathogens analysis. Comparison between 418 419 the inlet and the outlet pathogens concentrations is provided in Fig. 4a. The abundances 420 in secondary-treated effluent samples before treatment were $5.3 \pm 0.1 \log_{10} \text{MPN}/100$ 421 mL of E. coli, $4.6 \pm 0.1 \log_{10}$ MPN/100 mL of Enterococcus, $4.0 \pm 0.1 \log_{10}$ PFU/100 422 mL of *F*-specific RNA bacteriophages, and $3.5 \pm 0.2 \log_{10}$ CFU/100 mL of spores of 423 sulfite-reducing bacteria and are comparable to the values found in the literature 424 (Mandilara et al. 2006; Haramoto et al. 2015). When the effluent simply flowed through 425 FBC-CuO without PDS, the reduction of bacteria and parasite was very limited for E. 426 coli (0.2 log), Enterococcus (0.2 log), and spores of sulfite-reducing bacteria (0.3 log), 427 but for virus, a considerable reduction of *F*-specific RNA bacteriophages (2.7 log) was 428 observed. This was most likely a consequence of the presence at low concentration of 429 Cu(II) due to leaching from the surface of CuO pellets. As detailed in the next section, 430 this species, which presents well known biocidal characteristics, was identified by 431 suitable methods in the effluent at the column outlet.

432 In a similar way to the test carried out on antibiotics, the second step was initiated by 433 the addition of 500 µM of PDS to the inlet water tank and sampling started when the 434 permanent regime was reached. Prior to this experiment, and as already demonstrated 435 (Li et al. 2022) it was checked that PDS alone at ambient temperature had no 436 measurable effects on the abundances of pathogens. When the effluent flowed through 437 FBC-CuO with PDS, the reduction of 3 of the 4 pathogens indicators significantly 438 increased. E. coli (3.6 log) and F-specific RNA bacteriophages (3.8 log) were 439 respectively removed up to or just above the limit of detection. Enterococcus was also 440 significantly inactivated (1.3 log). However, the reduction of spores of sulfite-reducing *bacteria* (0.2 log, 38% abatement), the indicator representative of the parasite, was still 441

limited. Such pathogens are well identified in the literature as extremely difficult to
inactivate and resistant to disinfection processes, such as chlorination (Shields et al.
2008) and UV (Hijnen et al. 2006), but can alternatively be removed by low cost slow
sand filtration system (Timms et al. 1995).

446 Pathogens were ranked as E. coli and F-specific RNA bacteriophages > Enterococcus > spores of sulfite-reducing bacteria according to the treatment effectiveness criteria, and 447 448 was fully confirmed by the tests carried out at different flow rates (Fig. 4b). Spores were not inactivated by a process based on the combination of PDS and FBC-CuO, 449 450 whatever the operating conditions. At the opposite, the evolution of conversion rates 451 for the other three treatment-sensitive pathogens attested of the influence of operating 452 conditions. In such a process based on the coupling between kinetic of inactivation and 453 mass transport, an increase of the residence time almost systematically resulted in an increase of the conversion rates. Finally, the triplicate performed with a flow rate equal 454 455 for 1.5 mL/min brought to light the well-known uncertainty linked to the quantification of any pathogens populations, especially in the case of non-stabilized and non-456 457 controlled effluents such as STWW.

458 **3.4 Stability of FBC-CuO**

One of the essential characteristics for a catalyst to be a candidate for application in large-scale wastewater treatment is its stability and ability to maintain catalytic activity during long period of operation. Consequently, possible structural changes of the CuO pellet were evaluated by analyzing the catalyst recovered after all the measurement campaigns presented using SEM and X-ray diffractograms.

The SEM images of the surface of the millimetric CuO pellets were analyzed before and after the campaigns. The Fig. 5a and 5b highlighted that the surface was made off aggregates. A slight agglomeration of particles after treatment was observed, which may be due to the mechanism of PDS activation by CuO. This reaction that involved, during one step, an upper copper oxidation level, the cupryl ion (Li et al 2021), possibly led to additional local corrosion of CuO favorable to a slow and slight agglomeration phenomenon. However, in this study, no significant difference was obtained, with only slight changes from 623 ± 74 nm before treatment to 700 ± 30 nm after treatment, which indicated the good stability of surface morphology of CuO pellets.

The XRD diffractogram before and after treatment (Fig. 5c) shows well-defined and intense diffraction peaks located at the positions $2\Theta = 32.66, 35.63, 38.78, 46.37, 48.92,$ 53.61, 58.37, 61.70, 65.95, 66.39, 68.17 and 72.51. These peaks correspond to the monoclinic structure of CuO (Asbrink et al. 1991; Angi et al. 2014; Lanje et al. 2017). Lattice parameters were calculated and are a = 4.70 Å, b = 3.42 Å, c = 5.10 Å. The intensities, positions of the peaks and the lattice parameters are in good agreement with the reported values JCPDS file N°. 96-901-6058.

⁴⁸⁰ During disinfection trials in presence of PDS, stability of the catalyst was assessed ⁴⁸¹ against the leached concentration of Cu measured in solution by ICP-AES after a ⁴⁸² filtration step on 0.45 μ m cellulose filters (Fig. 5d). Even if non negligible, the Cu ⁴⁸³ leaching from CuO was limited and far less than that of 2 mg/L which is required by ⁴⁸⁴ environmental quality standards for surface water and by drinking water regulations ⁴⁸⁵ (WHO 2004).

Therefore, the results showed that the material presented phase purity and stability before and after treatment. The good stability and catalytic efficiency of CuO pellet at near neutral pH, make this system promising for application.

489

490 **4. Conclusions**

491 PDS activation by using CuO pellet as heterogeneous catalyst in a fixed-bed column 492 was applied for wastewater decontamination and disinfection. The first set of 493 experiments performed with a simple solution of phenol in distilled water have 494 demonstrated that this process, as any process based on the flowing of a reactive 495 mixture through a fixed packed bed was sensitive to operating conditions, especially 496 for flow rate and influent PDS concentration. FBC-CuO alone presented significant 497 removal performance on B-lactam and fluoroquinolones antibiotics through Cu(II) 498 complexation and degradation. But FBC-CuO alone demonstrated limited disinfection 499 performance. The combination of PDS with FBC-CuO was the necessary condition for 500 the degradation of SMX and CLA, not only improving the antibiotics degradation, but 501 also greatly enhancing the pathogens inactivation performances, excepted for spores of 502 sulfite-reducing bacteria, the indicator selected as representative of the parasites. It is 503 suggested that after the oxidative treatment, post-treatment by low-cost slow sand 504 filtration or ionized clay filtration, well adapted to parasites separation because of their 505 high characteristic size, may overcome the main limitations of this process. The 506 characterization comparison of CuO pellet before and after treatment and the 507 measurement of Cu(II) leaching demonstrated the excellent stability and reusability of 508 the CuO pellets.

509 Overall, it was shown that combination of PDS with FBC-CuO constitutes an efficient 510 and promising treatment option for the removal of micropollutants and microorganisms 511 from urban wastewater effluents.

512

513 Statements & Declarations

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518

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530 Availability of data and materials

531 The datasets used and analyzed during the current study are available from the

- 532 corresponding author on reasonable request.
- 533

534 Ethic approval

- 535 Not applicable.
- 536 **Consent to participate**
- 537 All authors have given consent to their contribution.
- 538 **Consent for publication**
- 539 All authors have agreed with the content and all have given consent to publish.

540

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705 Figures capation

Fig. 1. (a) Breakthrough curve of phenol in FBC-CuO; (b) phenol and PDS concentration profiles as a function of the time at the outlet of FBC-CuO; internal (c) phenol and (d) PDS concentration profiles in FBC-CuO. $C_{ph_i} = 5 \text{ mg/L}$, $C_{PDS_i} = 500$ μ M, flow rate = 3 mL/min.

- Fig. 2. The effect of different inlet PDS concentrations on outlet concentration profiles
- as a function of the time for (a) phenol and (c) PDS; on internal profiles when permanent
- regimes were reached for (b) phenol and (d) PDS. $C_{PDS_i} = 125,250,500$, and 1000 μ M,
- 713 $C_{ph_i} = 5 \text{ mg/L}$, flow rate = 3 mL/min.
- Fig. 3. Degradation of target antibiotics in DW and STWW by FBC-CuO alone: (a),
- 715 (c); and by FBC-CuO/PDS: (b), (d). $C_{AMX_i} = C_{CFX_i} = C_{OFL_i} = C_{SMX_i} = C_{CLA_i} = 250$
- 716 $\mu g/L$, $C_{PDS_i} = 500 \mu M$, flow rate = 1.5 mL/min.

Fig. 4. Pathogens enumerations in STWW before treatment at the inlet (BT) and after treatment at the outlet (AT) at a flow rate equal to 3 mL/min by FBC-CuO without and with PDS at a concentration $C_{PDS_i} = 500 \ \mu M$ (a), with PDS, same concentration and flow rates equal to 1.5, 3, and 9 mL/min. For 1.5 mL/min, triplicates were carried out and measurements variability are shown (for values above LOF). Note: * represents MPN for E. coli and Enterococcus, PFU for F-specific RNA bacteriophages, and CFU for spores of sulfite-reducing bacteria.

Fig. 5. SEM images of CuO pellet (a) before and (b) after treatment; (c) X-ray diffractograms of CuO pellet before and after treatment; (d) copper leaching at the outlet of the FBC-CuO in presence of PDS after 1 h and 4 h of flowing, $C_{PDS_i} = 500$ μ M, flow rate = 1.5 mL/min.



Fig. 1







Fig.2







Fig. 3







Fig. 4



Fig. 5