Journal of Environmental Chemical Engineering 3 (2015) 122–128

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Advanced treatment of urban wastewater by sand filtration and graphene adsorption for wastewater reuse: Effect on a mixture of pharmaceuticals and toxicity

L. Rizzo [a,*], A. Fiorentino [a], M. Grassi [b], D. Attanasio [a], M. Guida [c]

[a] Department of Civil Engineering, University of Salerno, Via Giovanni Paolo II, Fisciano, SA 84084, Italy
[b] Department of Civil and Environmental Engineering, University of Florence, Via di Santa Marta 3, Florence 50139, Italy
[c] Department of Biology, University of Naples Federico II, Complesso Universitario di Monte S. Angelo, Via Cinthia ed 7, Naples 80126, Italy

ARTICLE INFO

Article history:
Received 4 September 2014
Accepted 12 November 2014
Available online 14 November 2014

Keywords:
Agricultural wastewater reuse
Granular activated carbon
Carbon nanotubes
Pharmaceuticals
Phyto-toxicity tests
Sand filtration

ABSTRACT

Pharmaceuticals removal from urban wastewater by coupling conventional sand filtration with graphene adsorption reactor (GAR) was investigated. During GAR regime phase, the percentage removal of the four investigated pharmaceuticals, (namely caffeine, carbamazepine, ibuprofen and diclofenac) was higher than 95% (98.2, 97.0, 95.5 and 97.0%, respectively). In spite of the high initial concentrations of the target pharmaceuticals (10 mg/L each) and 4 months of experimentation (62 days of adsorption treatment), typical breakthrough adsorption curves were not observed. Graphene adsorption treatment effectively decreased toxicity to *Daphnia magna* (0–50% immobilization), but only a slight improvement in germination index (phyto-toxicity tests) was observed after GAR treatment. Finally, graphene performances were compared with conventional (granular activated carbon) adsorption process, and the best performance in the removal of pharmaceutical mixture was quite poor (62% in terms of UV absorbance) compared to GAR (96%).

Introduction

Persistent and bioactive contaminants, such as endocrine disruptor (EDs), pharmaceuticals and pesticides, also known as emerging contaminants (ECs), are continually introduced into the aquatic environment through different anthropogenic sources, and they can result in toxic and adverse effects on aquatic organisms and consequently on humans [1,2]. Among ECs, >200 different pharmaceuticals alone have been reported in river waters globally, and single compound acute toxicity testing (including crustaceans, algae and bacteria) have found median effective concentrations (EC50's) for a number of these ECs to be <1 mg/L [3]. Moreover, considering that they do not appear individually but as a complex mixture, additional adverse (synergistic) effects on aquatic organisms can be expected [4]. Unfortunately, their disposal into the environment is still unregulated, but EU legislation is expected to broaden to encompass municipal derived ECs among which some pharmaceutical [5].

Urban wastewater treatment plants (UWWTPs) effluents are among the major point sources of surface water contamination from ECs because of the poor efficiency of the conventional activated sludge process, the most used in UWWTPs [6,7]. In order to minimize (i) the release of ECs into the environment, (ii) effluent toxicity and (iii) the risk for consumer when effluent is reused for crop irrigation, UWWTPs should be upgraded with advanced treatment technologies. Different advanced technologies have been investigated in the removal of ECs from UWWTPs effluents, such as ozonation [8,9], advanced oxidation [10,11], membrane filtration [12,13], and adsorption [1,7,12,14]. But some drawbacks have been observed, for example: advanced oxidation processes (AOPs) can result in the formation of mostly unknown and sometimes toxic oxidation intermediates, if not properly operated [15], and membrane technology is quite expensive compared to other technologies. On the contrary, the adsorption process does not result in the formation of toxic by-products, and it is less expensive compared to membranes and AOPs. The most used adsorbent in wastewater treatment is activated carbon, which is commercially available as powdered activated carbon (PAC) and granular activated carbon (GAC). In a recent study, PAC adsorption was compared with ozonation process at a pilot scale to assess

* Corresponding author. Tel.: +39 89 969334; fax: +39 89 969620.
E-mail address: l.rizzo@unisa.it (L. Rizzo).

http://dx.doi.org/10.1016/j.jece.2014.11.011

Table 1
Average values of some parameters of wastewater samples taken from the effluent of the biological process of the UWWTP.

Parameter	Unit	Average value
pH	–	7.48
Total suspended solids	mg/L	29.5
BOD_5	mg/L	12
COD	mg/L	18.5
NH_3	mg/L	4.5
NO_{3-}	mg/L	16.9
NO_{2-}	mg/L	0.5
Alkalinity	mg $CaCO_3$/L	252
Conductivity	μS/cm	1105

their efficacy in removing ECs from secondary treated effluents as well as their effect on mutagenicity and genotoxicity of the treated wastewater [16]. PAC process was found to be less effective for the removal of most pharmaceuticals monitored but ozonation process increased mutagenicity and genotoxicity.

In this context, adsorption process looks like an interesting and attractive option for the advanced treatment of urban wastewater. Moreover, new adsorbents have been developed and investigated in the last years [17,18], also with potential application to urban wastewater treatment for the removal of ECs [14]. Among the new adsorbents, graphene based nanoadsorbents are attracting a huge interest [19]. Because of their small sizes, large surface area, high mechanical strength and remarkable electrical conductivities, they are potentially attractive for a wide range of applications in water treatment. Moreover, it is also evident from the scientific literature that there is a lack of data available on the adsorption of ECs by graphene and particularly from real wastewater [19]. Despite the higher cost compared to conventional adsorbents, several issues may contribute to make graphene adsorption a competitive technology for the next future, in particular: (i) more stringent legislation on urban wastewater disposal, (ii) further technology development (with expected decreased costs), (iii) higher specific surface area of graphene (which results in a lower volume for water treatment) and (iv) high expected process efficiency (which results in a lower regeneration frequency) with (v) lower effluent toxicity.

The main objective of this work was the investigation of ECs removal capacity by graphene adsorption from a real UWWTP effluent. In particular, four pharmaceuticals, namely caffeine, carbamazepine, ibuprofen and diclofenac, were used as model ECs (properties are reported in Supplementary Material, Table S1). Wastewater sample spiked with the target pharmaceuticals was first flowed through a sand filtration unit (SFU), to remove suspended solids, then through graphene adsorption reactor (GAR). Treatment efficiency was evaluated in terms of absorbance measurements, pharmaceutical compounds removal and toxicity tests. In order to evaluate possible agricultural reuse of treated wastewater, specific phyto-toxicity tests have been investigated. Finally, pharmaceuticals removal efficiency by graphene reactor was compared with a conventional GAC adsorption reactor.

Supplementry material related to this article found, in the online version, at http://dx.doi.org/10.1016/j.jece.2014.11.011.

Materials and methods

Materials

Caffeine, carbamazepine, ibuprofen and diclofenac (properties are reported in Supplementary Material, Table S1) and GAC (Norit PK 3-5) were purchased from Sigma–Aldrich. Methanol (Baker), acetonitrile (Carlo Erba) and phosphoric acid (Carlo Erba) were used for HPLC measurements. Aqueous solutions were prepared with deionized water (Milli-Q, Millipore).

Wastewater sample

Wastewater samples were taken in the effluent of the biological process (activated sludge), just upstream of the disinfection unit (chlorination) from a large UWWTP (250,000 equivalent inhabitants) located in southern Italy. The average values of some parameters of wastewater samples are given in Table 1.

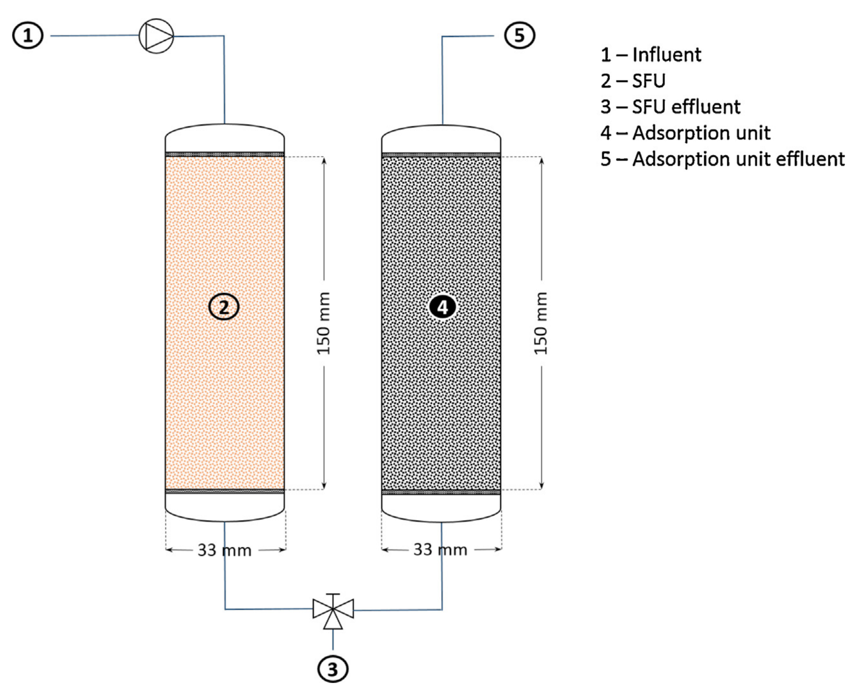

Fig. 1. Schematic representation of experimental set-up.