

Assessing the performance of an integrated column system containing zero valent iron nanoparticles and sodium persulfate solution for the removal of emerging contaminants from different wastewater matrices – Identification of transformation products

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Abstract The occurrence of micropollutants in the aquatic environment has raised the scientific concern because of their continuous discharge, their bioaccumulation and their potential adverse toxicological impacts on both aquatic organisms and human health. The present study has been focused in the assessment of the performance of an integrated column system in terms of the removal efficiency of selected micropollutants as a post-treatment step for different effluent matrices: an anaerobic membrane bioreactor (AnMBR), an upflow anaerobic sludge blanket reactor (UASB) followed by microfiltration, a sand filter after treatment of a septic tank followed by a saturated vertical wetland and a conventional tertiary treatment system. The system consists of a nanocomposite material, which is called R-nFe and includes zero-valent iron nanoparticles (nZVI) hosted into a strongly acidic cation exchange resin, and a sodium persulfate solution (PS) at a concentration of 1 mM, while the influent pH is acidic and the contact time 2.2 min. In addition, the transformation products of diclofenac and bisphenol A are being investigated. To the authors' best knowledge, this is the first time that the synergistic action of nZVI with PS is evaluated for the removal of micropollutants under continuous real wastewater flow with different matrix characteristics.

Keywords: micropollutants, nano zero valent iron, sodium persulfate, post-treatment, transformation products

1. Introduction

The presence of emerging contaminants or micropollutants (MPs) in water bodies has become an issue of great concern during the last decades. Their recalcitrant nature, their tendency to bioaccumulate and the acute and chronic toxicity that can influence

negatively both aquatic organisms and humans created the need of their control. Since wastewater treatment plants are one major way of entering into the environment because of their insufficient treatment through biological processes and filtration, more advanced treatment, such as advanced oxidation processes are being investigated.

The wide list of MPs includes pharmaceuticals and personal care products, pesticides, industrial chemicals, and their transformation products (TPs). Some of these chemicals can also cause endocrine disruptions and as such they are categorized as endocrine disrupting chemicals (EDCs). Furthermore, the TPs could be sometimes more persistent and more toxic than their parent compounds (Farré et al., 2008).

In this study, nZVI embedded within a cationic resin has been coupled with PS solution to trigger AOPs for the elimination of selected MPs from different effluent wastewater mediums performing column experiments. Ibuprofen (IBU), naproxen (NPX), diclofenac (DCF) and ketoprofen (KFN) have been selected as representatives of non-steroidal anti-inflammatory drugs (NSAIDs) category, while bisphenol a (BPA) of EDCs. In addition, the TPs of DCF and BPA have been investigated.

2. Materials and Methods

2.1. Materials

Sigma Aldrich (Steinheim, Germany) supplied IBU, NPX, DCF, KFN, BPA, meclofenamic acid sodium salt (MCF), deuterated bisphenol A (BPA-d16), ammonium formate, formic acid, ammonium acetate and sodium formate, all of high purity grade. They also provided resin Amberlyst 15 hydrogen form wet, pyridine and bis(trimethylsilyl)trifluoroacetamide (BSTFA) +1% trimethylchlorosilane (TMCS), HCl and sodium

persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) of high purity grade. Sodium chloride (NaCl) and iron chloride hexahydrate were obtained from Honeywell (Seelze, Hannover, Germany). Twining's of London (Swarzedz, Poland) was the green tea that used. Methanol and ethyl acetate of high-performance liquid chromatography grade were purchased from Merck (Darmstadt, Germany) and Honeywell, respectively. Ultrapure water was produced using a Milli-Q/Milli-RO Millipore system (Millipore, Billerica, MA, USA).

2.2. R-nFe synthesis

The nanocomposite material, namely R-nFe, was synthesized following an environmental friendly method developed by Toli et al., 2018. This involved embedding nano zero valent iron particles into the porous structure of a strongly acidic cation exchange resin using trivalent iron that is reduced to the elemental state by polyphenols found in green tea extract. Further details about the method can be found in Toli et al., 2018 and a pre-treatment step was performed prior to each experiment using a 1 M NaCl solution (100 g R-nFe/ 1 L NaCl), as suggested by Panagou et al., 2021.

2.3. Wastewater characteristics

The wastewater effluent matrices that were used as influent mediums in the R-nFe/PS system are: anaerobic membrane bioreactor (AnMBR), upflow anaerobic sludge blanket reactor (UASB) followed by microfiltration to avoid clogging of the R-nFe, sandfilter after treatment by septic tank and a saturated vertical flow wetland and a conventional tertiary treatment that included activated sludge system with nutrients removal, sandfiltration and UV disinfection. The main properties of the wastewater matrices used are summarized in Table 1.

Table 1. Wastewater main characteristics of the different effluent matrices used.

Parameter	AnMBR	UASB+ Microfiltration	Septic tank + Wetland + Sandfilter	Conventional tertiary treated
TSS (mg/L)	≤ 2	10 ± 3	7 ± 2	0.6 ± 0.2
CODt (mg/L)	91 ± 5	200 ± 10	36 ± 14	32.4 ± 1.2
TN (mg/L)	70 ± 4	75 ± 3	55 ± 2	8.1 ± 1
TP (mg/L)	6 ± 1	7.9 ± 2	5 ± 3	1.9 ± 0.5

2.4. Experimental protocol

To evaluate the efficiency of the R-nFe/PS system in removing selected MPs, column experiments were conducted at a downward flow of 26 L per day that achieved by a peristaltic pump. The feeding tank's influent pH was maintained at an acidic value of 3.5, and 200 g of R-nFe was used as the filler material, reaching

a height of 10 cm inside the column (inner diameter 5 cm). The contact time was 2.2 min which corresponded to an 11 min hydraulic retention time. In the case of conventional tertiary treated as influent matrix, a spike of 5 $\mu\text{g/L}$ was carried out. Each experimental run lasted for 5 days. The PS solution of 1 mM was supplied to the system with a use of a peristaltic pump at a rate of 0.84 mL/min. The configuration that was adopted in this study was based on our previous work (Barka et al., 2023).

Batch and column experiments were conducted for the identification of TPs of BPA and DCF. Ultrapure water was used as a matrix in both cases and initial pH was controlled (3.5). The initial compounds' concentration was 10 mg/L, much higher than the real ones found in the environment. However, this value was selected in order to facilitate the detection of TPs and the structure elucidation through an abundant and clear MS/MS spectra. Aliquots of 1 mL were withdrawn at zero time and at the end of each experiment and kept storage at -18°C until further analysis.

Batch tests performed with two Schott bottles of 1 L each, containing ultrapure water, PS 1 mM, DCF and BPA respectively. They were agitated at a speed of 200 rpm for approximately 2.5 min.

Column experiments for each compound separately took place using R-nFe alone and in combination with PS 1 mM. Contact time was 2.2 min and each column operated for 2 h.

2.5. Analytical methods

The method proposed by Samaras et al., 2011 was used to analyze the target MPs. The method involves filtering the samples, acidifying them to pH 2.5, adding surrogates (BPA-d16 for EDCs, MCF for NSAIDs), performing solid phase extraction, evaporating elutions to dryness under nitrogen purging, and then derivatization using 50 μL BSTFA+1% TMCS and 10 μL pyridine in a bath device at 70°C for 20 min. The final step is the injection (1 μL) in gas chromatograph (GC 7890A)-mass selective detector (MSD 5975C). The software Agilent ChemStation was used.

Ultra-high performance liquid chromatography (UHPLC, Dionex UltiMate 3000 RSLC, Thermo Fisher Scientific) coupled with a QToF mass spectrometer (Maxis Impact, Bruker Daltonics) used for the detection of TPs of BPA and DCF. The QToF-MS system had an electrospray ionization interface (ESI) source, which operated in both positive and negative ionization modes. The system recorded both data dependent and data independent high-resolution mass spectrometric (HRMS) spectra over a range of 50-1000 Da. Data Analysis 4.1, Metabolite Tools 2.0 and Target Analysis 1.3 Bruker Daltonics software packages (Bremen, Germany) were handled for mass spectra interpretation and data processing.

Both suspect and non-target screening approaches were followed for the identification of TPs.

3. Results and Discussion

3.1. R-nFe/PS performance with AnMBR effluent

The performance of the R-nFe/PS system when AnMBR effluent used appeared moderate to high for the target compounds (Figure 1). The highest removal efficiency was recorded for NPX (70%) and the lowest for BPA (54%). However, in terms of the mass removal of each substance per mass of R-nFe, the highest ratio obtained for IBU (5.4 µg IBU/g R-nFe). However, it should be noted that the initial concentration of the IBU was much higher (14,128±2,730 ng/L) than those of the other micropollutants which ranged from 951 ng/L (BPA) to 3,027 ng/L (DCF).

Augsburger et al., 2021 have also successfully used UV/H₂O₂ as a post-treatment step for the elimination of micropollutants in AnMBR effluent.

3.2. R-nFe/PS performance with filtered UASB effluent

The removal of the target MPs by the R-nFe/PS system when filtered UASB effluent used was moderate to low, as can be seen in Figure 1. Average removal efficiencies ranged from 34% (IBU) to 53% (DCF). The ratio of pollutant's mass removed per mass of R-nFe was quite similar for IBU, NPX, DCF and KFN (ranged from 0.40-0.54), while it was very low for BPA (0.07), which could be attributed to its low initial concentration (241 ng/L) in contrast to the initial concentration of the other compounds that ranged from 1,435 ng/L (NPX) to 1,838 ng/L (IBU).

Biological systems, such as high-rate algal ponds (Vassalle et al., 2020) have been used as post-treatment methods for micropollutants removal after UASB treatment. Regarding AOPs, only one study found in the literature which combines Fenton and photo-Fenton processes in UASB effluent and it has shown very promising results (Rodrigues-Silva et al., 2022). According to this study, the •OH radicals tend to attack the total organic carbon than the dissolved. The high total COD content in the UASB effluent could be an explanation for the low performance of the tested system towards the examined recalcitrant dissolved organics.

3.3. R-nFe/PS performance with sandfilter effluent

The treatment chain: septic tank, saturated vertical flow wetland, sandfilter and R-nFe/PS showed promising results for the removal of NPX (94%) and DCF (68%), which is also supported by the high ratio of pollutants' mass removed per mass of R-nFe (1.16 and 1.55 respectively), as also depicted in Figure 1. A moderate removal efficiency of 50% was recorded for BPA, while IBU and KFN seemed more recalcitrant. BPA's initial concentration was lower (802 ng/L) than the concentration of NSAIDs that ranged from 1,892 (NPX) to 3,516 ng/L (DCF). To the author's knowledge this is the first time that AOP is implemented as a polishing step after wetland treatment.

3.4. R-nFe/PS performance with conventional tertiary effluent

This experiment was included in the present study mainly for the purpose of comparing it with the other

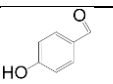
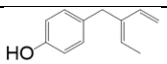
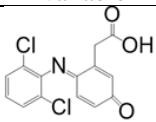
matrices. More than 70% removal efficiency achieved for all the tested compounds, except KFN (Figure 1). The refractory nature of KFN was also indicated by the low ratio of its mass removed per mass of R-nFe (0.85), while this ratio was higher than 2.3 for the other compounds. The predominant removal mechanisms assumed for the tested MPs in this study were oxidation by sulfate and hydroxyl radicals, with adsorption also playing a potentially important role.

The low levels of COD, TSS and nutrients in the wastewater matrix had a positive impact on the removal of these trace organics. Especially for MPs of moderate to low biodegradability the low content of readily available carbon was found to be a critical factor in their successful removal (Kahl et al., 2017). In addition, the occurrence of inorganic substances, such as Cl⁻, NO₃⁻, HCO₃⁻, SO₄²⁻ and PO₄³⁻, and soluble organic matter was observed to scavenge radicals (Wu et al., 2020).

3.5. TPs identification

Overall, twelve TPs of BPA were detected and five of them were structurally elucidated, while nine TPs were detected for DCF and possible structures were proposed for almost all of them. In Table 2, those TPs that correspond to column tests are being presented.

Table 2. TPs identified in column tests.

TP	Workf low	Proposed chemical formula	Proposed structure	Ref .
BPA-122	Suspect	C ₇ H ₆ O ₂		a
BPA-174	Non-target	C ₁₂ H ₁₄ O		
BPA-324B	Non-target	Not Available	Not Available	
BPA-382	Non-target	Not Available	Not Available	
BPA-457	Non-target	Not Available	Not Available	
BPA-515	Non-target	Not Available	Not Available	
BPA-441	Non-target	Not Available	Not Available	
DCF-309*	Suspect	C ₁₄ H ₉ Cl ₂ NO ₃		b
DCF-228	Non-target	Not Available	Not Available	

*It was detected only when PS added.

a. (Li et al., 2022)

b. (Monteagudo et al., 2018)

4. Conclusions

With respect to removal of the target MPs, the R-nFe/PS system exhibited better performance for the tested

effluent matrices in the descending order of: conventional tertiary treated > AnMBR > septic tank + wetland + sandfilter > UASB + microfiltration. The low content of COD, TSS and nutrients is expected to play an important role for the successful performance of the R-nFe/PS system.

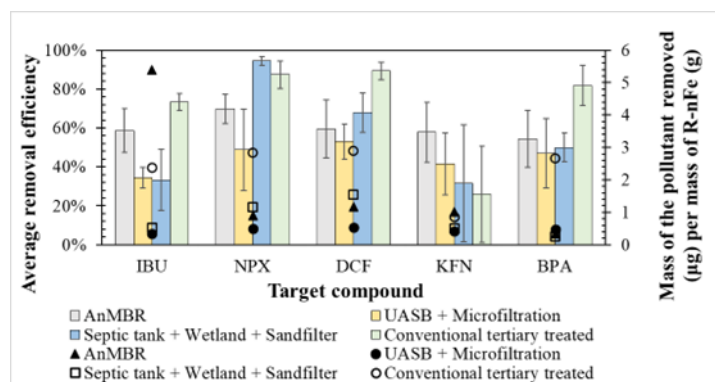


Figure 1. The performance of the R-nFe/PS system in terms of the removal of the target micropollutants towards different wastewater effluent matrices.

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