The improvement of removal effects on organic pollutants in Wastewater Treatment Plants (WWTP)

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Abstract. Purpose of this study is to improve the efficiency of removal in wastewater treatment plants of some organic pollutants like pharmaceuticals, antioxidants, pesticides (triazines, phenylurea herbicides), personal care products (PCPs) musk fragrances (galaxolide and tonalide) and estrogens using zeolites with excellent absorption capacity. The zeolite selected for all experiments was Szedimentin-MW. The experiment took place in three stages: no zeolite addition, zeolite added at the end of the bioreactor and zeolite added at the start of the bioreactor. The water samples were pre-concentrated with solid phase extraction (SPE) procedure and analyzed with analytical system Gas Chromatography/Mass Spectrometry (GC/MS).

1. Introduction

Wastewater treatment systems have been designed to minimize the environmental impacts of discharging untreated wastewater. The choose of solutions for wastewater treatment lead to different performance in pollutants removal and therefore to different impacts on the environment [1].

In the recent decades, the increase in human population brought about increased quantity of wastewaters and increased demands on the quality of wastewater treatment products, the effluent and sewage sludge [2].

Persistent pollutants like pharmaceuticals, antioxidants, pesticides (triazines, phenylurea herbicides), musk fragrances (galaxolide and tonalide) and estrogens are very frequent detected in industrial and domestic wastewater and show great damage to environment. In recent years, interest has been focused on the removal of this organic pollutants from aqueous/sludge systems.

The widespread presence of pharmaceuticals and personale care products in the aquatic environment can be explained by their extensively us in medical practices and incomplete removal in Wastewater Treatment Plant (WWTP). Their annual consummation ranges between a few kilograms and several hundred tons per individual compounds.

It is assumed that PCPs could act as persistent compounds, because of their continual discharge into aquatic media via WWTP effluents, which sustain a multigenerational exposure for the resident organisms.
Also, the polycyclic synthetic musk as Galaxolide (HHCB) and Tonalide (AHTN) has large applications as fragrances in soaps, perfumes, air fresheners, detergents, fabric softener and other cleaning products. There are indications that the polycyclic musks are not only to be found in various environmental compartments but also in the aquatic food chain as well as in fatty tissue and mothers’ milk [3].

Zeolite is one of the excellent substances with a great absorption capacity, which is produced at mines naturally, and is also synthesized by artificial process. There are various types of zeolite by its crystal structure. Zeolite itself is often utilized as water purification material for its incomparable ion-exchange capacity [4].

They have been used as adsorbents, molecular sieves, membranes, ion exchanger and catalysts in municipal and industrial pollution control, as well as in horticulture, agriculture, and environmental soil remediation but their primary use has been in water and wastewater treatment [5].

Zeolite refers to a group of minerals that are basically hydrated calcium potassium sodium aluminosilicates in which the water is held in cavities in the lattice. The lattices are negatively charge and they loosely hold cations. Their ability to exchange one cation for another is known as their “cation-exchange capacity” or “CEC”. Total cation-exchange capacities in natural zeolites vary from 25 to 300 meq/100 g [6].

The present paper concern is the study of removal efficiency of Szedimentin-MW zeolite on few class of compounds early described, in WWTP serving an equivalent population of 300.000 (Varna, Bulgaria). The water samples were pre-concentrated with solid phase extraction (SPE) procedure and analyzed with analytical system Gas Chromatography/Mass Spectrometry (GC/MS).

2. Experimental

The full-scale experiments have dual purpose: optimisation of the dose of zeolite (experiments at various concentrations) and the zeolite dosing points.

The simplified scheme of experimental WWTP is shown in figure 1:

![Figure 1. Scheme of WWTP. Stream 3: Dose to maintain 7.5 % concentration of zeolite in the activated sludge. Stream 2: Dose to maintain 5.0 % concentration of zeolite in the activated sludge. Stream 1: Reference stream. 0 % concentration of zeolite in the activated sludge. Zeolite dosing points: Stream 1 – No zeolite addition; Stream 2 – Zeolite added at the end of the bioreactor; Stream 3 – Zeolite added at the start of the bioreactor.]

The parameters of the experiments were: Sludge concentration in the bioreactor: 2.0 to 2.8 g/L and in the recycled sludge: 3.0 to 4.2 g/L. The sludge retention time was 8 days on average and the hydraulic retention time 10 hours on average, 3-4 hours at peak loads (no inlet buffer tank). The measurements of selected compounds were done in three consecutive days.

2.1. Reagents and materials

All solvents were of HPLC grade. Dichloromethane was purchased from JT Baker (Deventer, Holland). Acetonitrile, Methanol, HPLC Water and Isooctane from Merck (Darmstadt, Germany). Glass microfiber filters (GF 6, Ø 47 mm, Lot EU0940-1) were obtained from Whatman (Dassel,
Germany). The OASIS HLB 3cc cartridge containing the 30 mg macroporous copolymer [poly(divinylbenzene-co-N-vinylpyrrolidone)], was purchased from Waters Corporation (Milford, Mass USA).

2.2. Instrumentation
A Thermo Finnigan Trace GC interfaced with a Polaris Q ion trap mass spectrometer was used for all samples. The gas chromatograph was equipped with a (5%-Phenyl)-methylpolysiloxane GC column (HP-5MS column, 30 m x 0.25 mm i.d., 0.25 µm film thickness) purchased from Agilent Technologies (Santa Clara, U.S.A.). The conditions of the analysis were as follows: injection volume (2.0 µl) with splitless injection, injector temperature: 280ºC and transfer line temperature: 300ºC. The carrier gas was helium with flow rate of 2 ml/min at constant flow with vacuum compensation. The temperature programme: the initial temperature was 80ºC (1 min), than increased to 150ºC at 15ºC/min, to 192ºC at 3ºC/min, to 193ºC at 0.2ºC/min and to 300ºC at the rate of 10ºC/min, where it was held for 10 min.

2.3. Solid phase extraction method
The most common sample preparation for trace analysis of organic pollutants in water involves solid-phase-extraction (SPE). The extraction efficiency of SPE is found to be higher than the traditional liquid–liquid extraction [7].

In our research, we used for extraction, the OASIS HLB cartridge described in section 2.1. The samples were acidified with 2 N HCl to pH 2 and filtrated on a glass fibre filter.

2.3.1. SPE procedure
The divinylbenzene/N-vinylpyrrolidone copolymer SPE cartridge (Oasis HLB) was prewashed with methanol and organic-free water with the flow rate of 2 ml/min. The water sample was then percolated through the cartridge with a flow rate of 3-5 ml/min under vacuum. Finally, after drying, the cartridge was eluted with methanol [8].

After elution the extract was concentrated by rotavapor system and transferred into isooctane. The final extract was transferred to vials and the excess of solvent was evaporated under a stream of dry nitrogen. The samples were injected (2 µl of sample in iso-octane) in the GC/MS system without derivatization.

3. Results and discussion
GC conditions allowed the complete separation of the target compounds.

Table 1. Concentration of antioxidants (1,2), triazines (3-6), phenyl urea herbicides (7,8), fragrances (9), antimicrobials (10) and antiepileptic drugs (11) in ng/l. The symbol (*) is for concentration under LOQ, (**) the symbol BHA and BHT denoted the compounds Buthylhydroxyanisole and Buthylhydroxytoluene respectively.

| Nr.  | Compound     | LOQ (ng/l) | Day 1 | Day 2 | Day 3 |
|------|--------------|------------|-------|-------|-------|
|      |              |            | P0    | P1    | P2    |
| 1    | BHA**        | 30         | 824   | 717   | 825   |
| 2    | BHT**        | 30         | 560   | 343   | 220   |
| 3    | Prometon     | 7          | *     | *     | *     |
| 4    | Atrazin      | 40         | *     | *     | *     |
| 5    | Propazin     | 13         | *     | *     | *     |
| 6    | Ametrin      | 30         | *     | *     | *     |
| 7    | Diuron       | 20         | *     | *     | *     |
| 8    | Isoproturon  | 7          | *     | *     | *     |
| 9    | Tonalide     | 15         | 251   | 349   | 150   |
| 10   | Triclosan    | 7          | 762   | 264   | 476   |
| 11   | Carbamazepine| 10         | 72    | 77    | 77    |
Quantities were calculated using the chromatographic area obtained in the full scan mode. It has been used as internal surrogate standard Diphenylamine in concentration of 1000 ng/L. The results obtained are shown in table 1.

We observe that:
- the concentrations of compounds in P1 was close to P0 (except for triclosan in day 1);
- the concentrations of compounds in P2 was around of 72% in day 1, 87% in day 2 and 85% in day 3 (relative to P0);
- the concentrations of compounds in P3 was around of 62% in day 1, 69% in day 2 and 76% in day 3 (relative to P0);
- the minimum of concentration was observed for BHT day 1, point 3 (16%) and triclosan, day 1, point 3 (28 %);
- in all situation carbamazepine was observed in concentration close to P0;

the results shown that more best retention was in the point 3, day 1.

4. Conclusions
For stream 2 (9 g/mc) we observe an average removal quantity of 19%. For stream 3 (15 g/mc) we observe an average removal quantity of 31%. To increase the efficiency of removal we observe that is good to use a big amount of zeolite (> 15g/mc), added at the start of the bioreactor. In all situation carbamazepine removal was 0%. Removal quantity was related to stream 1 (no zeolite added). The studied waste water originate main from domestic activity. This is the explanation of the fact that in all samples pesticides classes was not detected.

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