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Pre-treatment of hospital wastewater by coagulation–flocculation and flotation

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ABSTRACT

Coagulation–flocculation and flotation processes were evaluated for the pre-treatment of hospital wastewater, including the removal of 13 pharmaceutical and personal care products (PPCPs). Coagulation–flocculation assays were performed in a Jar-Test device and in a continuous pilot-scale plant. Raw hospital wastewater as well as the effluent from the continuous coagulation plant were treated in a flotation cell. Removal of total suspended solids (TSS) during pre-treatment was very effective, reaching an average removal efficiency of 92% in the combined coagulation–flotation process. Musk fragrances were eliminated to a high degree during batch coagulation–flocculation (tonalide: 83.4 ± 14.3%; galaxolide: 79.2 ± 9.9%; celestolide: 77.7 ± 16.8%), presumably due to their strong lipophilic character which promotes the interaction of these compounds with the lipid fraction of solids. For diclofenac (DCF), naproxen (NPX) and ibuprofen (IBP) maximum removals of 46%, 42% and 23%, respectively, were obtained, while the rest of PPCPs were not affected by the physico-chemical treatment. Flotation of raw wastewater led to slightly worse results compared to coagulation–flocculation, although the combined action of both improved the overall efficiency of the process. The proposed pre-treatment strategy for hospital wastewater is useful for assimilating its conventional physico-chemical characteristics to that of municipal wastewater as well as for reducing the load of some PPCPs into the sewer system.

1. Introduction

Coagulation–flocculation and flotation are physico-chemical processes that can be applied at different stages of water treatment: (i) pre-treatment of industrial effluents before entering municipal sewer systems (Jain et al., 2001; Liu and Lien, 2001; Gautam et al., 2007); (ii) primary treatment of urban wastewater (Mels et al., 2001); (iii) tertiary treatment of urban wastewater (Chuang et al., 2006); and (iv) drinking water treatment plants, which typically combine coagulation with sand filtration, sorption by activated carbon and disinfection by ozone or chlorine.

Very little information is available so far concerning the fate and behaviour of emerging xenobiotic micropollutants present in sewage, such as pharmaceuticals, hormones, etc., during coagulation or flotation processes. Several works have been published during the last years dealing with the occurrence of pharmaceutical and personal care products (PPCPs) during coagulation–flocculation steps in drinking water plants (Adams et al., 2002; Westerhoff et al., 2005; Seitz et al., 2006; Vieno et al., 2006; Stackelberg et al., 2007) as well during primary treatment of municipal wastewater (Carballa et al., 2005). Regarding pre-treatment of industrial effluents that may represent important sources of pharmaceuticals in wastewaters, as pharmaceutical manufacturing companies and hospitals, information is also scarce and merely focussed on conventional parameters, such as chemical oxygen demand (COD), total suspended solids (TSS) and pathogens (Torres et al., 1997; Chiang et al., 2003; Kajitvichyanukul and Suntronvipart, 2006; Gautam et al., 2007).

Hospitals are known to be intensive consumers of water, thus generating significantly higher wastewater flows than conventional households (400–1200 L bed^{-1} d^{-1} (Gautam et al., 2007) vs. 100 L $capita^{-1}$ d^{-1}). Moreover, hospital effluents constitute a very complex water matrix, loaded with microorganisms, heavy metals, pharmaceuticals, toxic chemicals and radioactive elements. The direct discharge of these effluents into urban sewerage systems without preliminary treatment, constitutes a potential risk to the environment, since conventional sewage treatment plants (STPs) have not been really designed for this specific purpose.

Cytostatic agents (ifosfamide and cyclophosphamide) belong to the group of pharmaceuticals which are specifically consumed in hospitals, although a fraction of the administered dose could be excreted at home by out-patients. Expected concentrations in hospital effluents are in the range of 5–50 μg L^{-1}, although a high variability has been observed (Kummerer, 2001). According to the information gathered between 1997 and 2002 in 15 European countries, hospital care consumption as a proportion of total antibiotic consumption can be quite significant ranging from 6.4% up to 17.8% (Vander Stichele et al., 2006). This proportion was reported to be as high as 26% in Germany, which appears to be the

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cause of the high concentrations (up to 100 μg L^{-1}) reported for several antibiotics, such as β-lactams, fluoroquinolones, sulfonamides and trimethoprim in different German hospital effluents (Kummerer, 2001; Lindberg et al., 2004; Brown et al., 2006). Hospital can neither be neglected as contributors of adsorbable organic halogen compounds (AOX) in urban wastewaters, contained in X-ray contrast media, solvents, disinfectants, cleaners and drugs containing chlorine (Kummerer, 2001).

The purpose of this work is to study the suitability of coagulation-flocculation and flotation processes for the pre-treatment of hospital wastewater, especially focussing on the removal of 13 PPCPs which have been chosen as representative ingredients belonging to different therapeutic groups highly consumed in modern societies, as well as substances with different physicochemical properties (Suarez et al., 2008). The final selection was composed of three musk compounds (galaxolide (HHCB), tonalide (AHTN) and celestolide (ADBI)), the anti-epileptic carbamazepine (CBZ), the tranquiliser diazepam (DZP), three anti-inflammatory drugs (ibuprofen (IBP), naproxen (NPX) and diclofenac (DCF)), four antibiotics (sulfamethoxazole (SMX), roxithromycin (ROX), trimethoprim (TMP) and erythromicyn (ERY)) and the iodinated contrast media iopromide (IPM).

2. Methods

2.1. Wastewater

Batch coagulation–flocculation and flotation experiments were carried out with wastewater collected during two sampling campaigns (November 2005 and March 2006) at a hospital of around 750 beds and outpatient consultation for all medical specialties that generates a wastewater flow of 429 ± 63 m^3 d^{-1}. Two types of hospital streams were considered: S1 which comprises wastewater from hospitalised patients, surgery, laboratories, radiology and general services; and S2 which consists of wastewater from radiotherapy and outpatient consultation (Table 1).

2.2. Batch coagulation–flocculation experiments

Batch coagulation–flocculation experiments were carried out in a Jar-Test device, in four 1-L glass beakers. Two types of coagulants were considered, namely ferric chloride ($FeCl_3$) and aluminium sulphate ($Al_2(SO_4)_3$).

The experimental procedure started with the filling of beakers with 850 mL of hospital wastewater, which were spiked with PPCPs at the following concentrations: 10 μg L^{-1} of DCF and antibiotics; 20 μg L^{-1} of CBZ and DZP and 40 μg L^{-1} of fragrances. For the spike, stock solutions of each PPCPs at a concentration of 2000 mg L^{-1} were prepared by dissolving the commercially available reagents (Sigma–Aldrich, Fluka and Ventos) in methanol or acetone. The compounds IPM, IBP and NPX were not included in the spike since relatively high concentrations were already detected in the analyses performed on the wastewater matrix (Table 1). The corresponding dose of coagulant and alkalinity was added to each vessel, with the exception of the blank where the assay was run in the absence of external reagents.

The experiment consisted of the following sequential steps: (i) coagulation: fast stirring at 150 rpm during 3 min; (ii) flocculation: gentle stirring at 50 rpm during 5 min; (iii) settling: stirrers were switched off in order to allow settling of flocs during 1 h; and (iv) sampling: the supernatant was analysed to determine TSS, total COD and PPCP concentrations.

Table 1
Characteristics of hospital wastewater used for batch experiments, including conventional parameters (in mg L^{-1}) and detected PPCPs (in μg L^{-1}).

Wastewater sample	TSS	COD_T	COD_S	pH	Fat
S1 Nov. 2005	339	2464	2277	7.9	43
S2 Nov. 2005	225	504	164	7.4	13
S1 March 2006	136	540	280	8.7	25
S2 March 2006	67	375	220	8.5	9
	IBP	NPX	HHCB	AHTN	IPM
S1 Nov. 2005	21.7	12.6	2.57	1.61	1400
S2 Nov. 2005	74.7	18.1	0.79	0.38	260
S1 March 2006	20.3	6.9	0.81	0.68	1350
S2 March 2006	10.8	3.9	0.41	0.65	55

2.3. Batch flotation experiments

Dissolved air flotation assays were performed in a device composed of a 2-L pressurisation cell, where tap water was saturated with air at high pressure (5–6 bar), connected to a 1 L flotation cell that contained the wastewater sample to be treated (Fig. 1A). Same conditions regarding types and doses of coagulants and alkalinity as in the previous experiments were considered.

The experiment comprised: (i) sample preparation: Hospital effluents were spiked with the same PPCPs mixture to attain the same concentrations as in the previous experiments. A volume of 700 mL was transferred to the flotation cell and supplied with the corresponding doses of coagulants and alkalinity, with the exception of the blank; (ii) saturation: pressurisation cell was filled with water that was afterwards saturated with air; (iii) flotation: 200 mL of saturated water were introduced at the bottom of the flotation cell and flotation of suspended solids and fat was allowed to occur for 1 h; and (iv) sampling: a syringe was used to obtain a sample from below the water surface, in order to avoid the floating layer, to analyse TSS, total COD and PPCP concentrations.

2.4. Coagulation–flocculation pilot plant

Hospital wastewater was always collected as a mixture of streams S1 and S2 the day before each experiment was run. Once the desired volume was obtained, it was spiked with PPCPs following the same procedure as previously indicated and left under continuous stirring during the whole night in order to attain complete homogenisation. Afterwards it was continuously fed to the coagulation–flocculation pilot plant.

The pilot plant used consisted of three main sections (Fig. 1B): (i) coagulation tank of around 4.4 L equipped with a fixed-speed stirrer (200 rpm); (ii) flocculation tank with a volume of 15 L provided with a speed-regulated stirrer (25 rpm maximum); and (iii) lamellar settler composed of 10 stainless steel (AISI-304) plates in a 35-L tank.

The system was operated at a hydraulic retention time (HRT) of 32 min (12 min of coagulation–flocculation plus 20 min of settling), with continuous addition of hospital wastewater and the selected coagulant ($FeCl_3$ or $Al_2(SO_4)_3$). After 90 min of steady operation of the pilot plant (corresponding to 3 HRT), the effluent was sampled in order to analyse conventional parameters as well as PPCP concentrations. Operational conditions were selected after analysing the results previously obtained in batch experiments in order to optimise the selection of coagulant and its dose. In all cases, operation was carried out twice during two consecutive weeks.

2.5. Operation strategy

Optimum doses for coagulants in preliminary Jar-Test experiments were selected in which only removal of TSS was analysed as a function of $FeCl_3$ and $Al_2(SO_4)_3$ additions in the range 0–200 ppm. Additionally, the need of alkalinity addition in the form

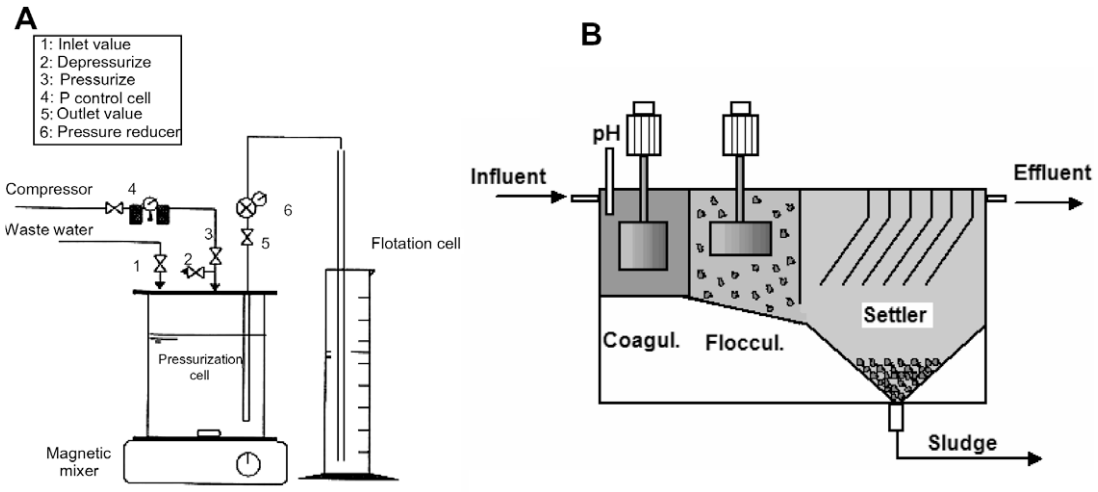

Fig. 1. (A) Flotation cell; and (B) coagulation–flocculation pilot plant used for the experiments.

of $NaCO_3$ in order to avoid a possible drop in pH was evaluated (Gautam et al., 2007). Stock solutions of $FeCl_3$, $Al_2(SO_4)_3$ and $NaCO_3$ in Milli-Q water at a concentration of 40 g L^{-1} were used for these experiments. It was observed that only coagulant additions above 25 mg L^{-1} required a supplement of $NaCO_3$ at the same dose as the coagulant. Furthermore, coagulant doses above 50 mg L^{-1} did not lead to an additional improvement in the separation process, thus this concentration was selected as the maximum addition to be considered in further assays.

Four sets of batch coagulation–flocculation and flotation assays were performed considering the following operation conditions: (i) absence of reagents; (ii) 25 mg L^{-1} of $FeCl_3$; (iii) 50 mg L^{-1} of $FeCl_3$ and of $NaCO_3$; (iv) 25 mg L^{-1} of $Al_2(SO_4)_3$; and (v) 50 mg L^{-1} of $Al_2(SO_4)_3$ and of $NaCO_3$.

Continuous pilot plant experiments have been only conducted in the absence of reagents and at the lower coagulant dose (25 mg L^{-1} of $FeCl_3$ and 25 mg L^{-1} of $Al_2(SO_4)_3$), since batch experiments revealed that working at higher doses did not improve the process.

The effluent of this pilot plant was afterwards treated in the flotation cell in order to compare two possible pre-treatment strategies for hospital effluents: (i) single coagulation–flocculation unit; and (ii) two-step treatment by coagulation–flocculation followed by flotation.

2.6. Analytical methods

Samples were collected in glass or aluminium bottles. A small fraction was taken for the determination of TSS and COD on the unfiltered samples following standard methods (APHA-AWWA-WPCF, 1999), while the rest was immediately prefiltered (AP4004705, Millipore). The analysis of antibiotics and iopromide was carried out in the Austrian Federal Environment Agency where an analytical method for the detection of such compounds by LC–MS–MS is available. The preservation of those samples was guaranteed by adding a pinch of sodium azide and freezing them until being analysed. For the rest of compounds, samples were analysed within one week, thus storage in the fridge was sufficient.

The analysis of soluble content of anti-inflammatory compounds, CBZ, DZP and musks started with the preparation of the sample by adjusting its pH to 2.5 and adding meclofenamic acid and dihydrocarbamazepine as surrogate standards. Afterwards the samples were pre-concentrated by solid-phase extraction (SPE) of 250 mL samples through 60 mg OASIS HLB cartridges (Waters, Milford, MA, USA) followed by elution from the cartridge using 3 mL of ethyl acetate. This extract was divided into two fractions: one of them was used for direct determination of CBZ, DZP, HHCB, AHTN and ADBI, while the other one was employed for the analysis of anti-inflammatories as their tertbutyldimethylsilyl derivatives (Rodríguez et al., 2003). GC/MS detection was carried out in a Varian CP 3900 chromatograph (Walnut Creek, CA, USA) equipped with a split–splitless injector and connected to an ion-trap mass spectrometer. Additionally, total concentrations of musks were determined by solid phase micro extraction (SPME) following the procedure developed by García-Jares et al. (2002). Briefly, 10-mL samples were immersed in a bath at 100 °C for 5 min to equilibrate temperature. Then, a PDMS-DVB fibre (65 μm polydimethylsiloxane-diviylbenzene, Supelco, USA) was exposed to the headspace over the sample for 25 min. Once the exposition finished, the fibre was immediately inserted into the GC injector for chromatographic analysis. Desorption time was set at 2 min, although an extra period of 5 min was considered to avoid carryover effects.

For analysis of antibiotics and iopromide, sulfadimidin-C13 and Caffeine-C13 were used as internal standards and an acidic buffer solution was added to the samples prior to sample extraction. SPE was carried out with Isolute 101 cartridges and analytes were eluted with methanol and acidic methanol. Final detection was performed in a LC–MS–MS in the positive ESI mode.

2.7. Calculations

Removal efficiencies (E_j) for TSS, COD and PPCPs were determined according to Eq. (1):

$$E_j = \frac{C_{j,Influent} - C_{j,Effluent}}{C_{j,Influent}} \cdot 100 \quad (1)$$

where, $C_{j,Influent}$ and $C_{j,Effluent}$ are the concentrations of compound j (mg L^{-1} or μg L^{-1}) in the influent and effluent, respectively.

Calculations were based on soluble concentrations of PPCPs, except for fragrances and DCF for which total concentrations have been considered in the analysis, according to their higher sorption potential (Suarez et al., 2008). In the case of DCF, total concentrations ($C_{j,total}$ in μg L^{-1}) were determined applying Eq. (2):

$$C_{j,total} = C_{j,dissolved} \cdot (1 + K_{d,j} \cdot SS) \quad (2)$$

where, $C_{j,dissolved}$ is the soluble concentration of compound j (μg L^{-1}), $K_{d,j}$ its solid–water distribution coefficient (L/kg) and SS the

suspended solids content (kg L^{-1}) of the considered stream (influent or effluent). Sorption coeffients ($K_{d,j}$) for fragrances have been determined from experimentally measured total and soluble concentrations, whereas for DCF the value of 459 L/kg reported by Ternes et al. (2004) for primary sludge was considered.

The theoretical removal efficiency expected for fragrances and DCF due to sorption onto solids was determined with the following equation:

$$Removal\ (\%) = \frac{K_d \cdot SS}{1 + K_d \cdot SS} \cdot E_{rss} \quad (3)$$

where E_{TSS} is the efficiency of pre-treatment regarding TSS removal (%).

3. Results and discussion

3.1. Batch coagulation–flocculation experiments

Coagulation–flocculation processes have been designed for promoting removal of suspended solids and colloids from wastewater, which do not settle spontaneously. Typically, removal of TSS could be increased from 40–70% without coagulation up to 60–90% if a coagulant is used (Vesilind, 2003). In the case of the hospital wastewaters considered in this work, suspended particles already showed good settling properties without external addition of coagulants (69–84%), which was somewhat enhanced (4–13%) when the wastewater was coagulated with $FeCl_3$ (Fig. 2). The second additive considered ($Al_2(SO_4)_3$) led to an increase in TSS in the effluent when compared to the blank. Hence, the use of aluminium salts was less favourable concerning conventional wastewater pollutants.

Removal of COD was highly influenced by the fraction of total COD associated to particulate and soluble organic matter. 11–18% COD was removed in the sample obtained from stream S1 in November 2005 (Fig. 2a), which contained only 8% of total COD associated to solid particles; whereas higher removals were achieved (up to 72%) for stream S1 in March 2006 (Fig. 2c), for which 38% of its total COD was associated to solids. If optimal operation conditions had to be selected on the basis of conventional wastewater parameters, it would correspond to the use of 50 mg L^{-1} of $FeCl_3$ as coagulation agent.

Table 2 shows the removals of PPCPs achieved in Jar-Test assays. In general, the compounds IPM, CBZ, DZP and IBP were not eliminated from the liquid phase during the process, with the exception of the experiment carried out with stream S1 in March 2006, where a maximum decrease in the concentration of CBZ and DZP of more than 40% was obtained. These values are in concordance with the low sorption tendency expected for these compounds according to their sorption coefficients reported for primary sludge (K_d < 44 L/kg, Ternes et al., 2004). The ineffectiveness of coagulation processes for the removal of CBZ and IBP in drinking water treatment plants as well as during primary treatment of municipal sewage has been reported by several authors (Ternes et al., 2002; Carballa et al., 2005; Vieno et al., 2006). Similarly, IPM showed to be very resistant to coagulation–flocculation during drinking water treatment (Westerhoff et al., 2005; Seitz et al., 2006). Maximum removal of DZP during primary treatment did not exceed 25% even when using much higher coagulant doses than those considered in the present work (Carballa et al., 2005).

Removal of NPX was in the range of 10–40% (Table 2), which was somewhat higher than some previously reported data for primary treatment (Carballa et al., 2005) and for drinking water treatment (Boyd et al., 2003; Westerhoff et al., 2005). This anti-inflammatory drug is negatively charged at the circum-neutral pH of the wastewater (pK_a 4.2), therefore electrostatic interactions with the negatively charged surface of suspended solids (commonly referred to as adsorption) are discarded, unless this negative charge could be previously neutralised as it is expected to occur with the trivalent cations released by the coagulant. However, the similar results obtained in blank assays are difficult to explain. One possible explanation is that the presence of heavy metals such as Pt^{+4} or Gd^{+3}, commonly reported in hospital effluents (Kummerer, 2004), could exert a similar effect as trivalent cations.

Negative removals were observed for macrolides (ROX and ERY) and trimethoprim during coagulation, whereas SMX concentrations were not significantly altered. For the sulphonamide, the ineffectiveness of coagulation processes had already been reported for drinking water treatment (Adams et al., 2002; Vieno et al.,

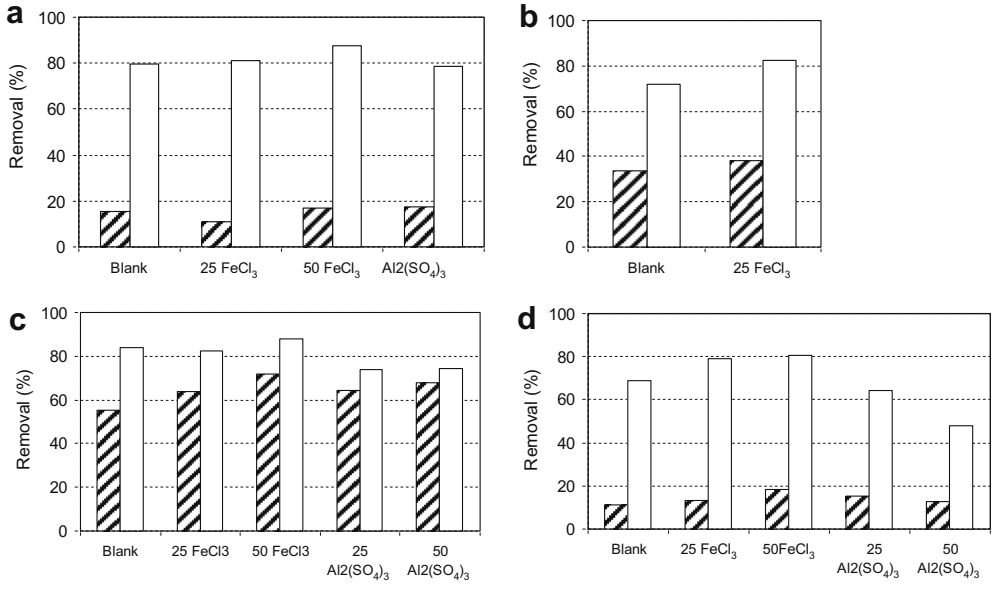

Fig. 2. Removal of total COD (▨) and TSS (□) during batch coagulation–flocculation of hospital wastewater: (a) S1; (b) S2 from November 2005; (c) S1; and (d) S2 from March 2006.

Table 2
Removal of PPCPs (%) during batch coagulation-flocculation and flotation of hospital wastewater. Operational conditions during which maximum removals were achieved.

PPCP	Coagulation–flocculation			Flotation		
	Mean ± standard deviation	Range	Optimum coagulant dose	Mean ± standard deviation	Range	Optimum coagulant dose
AHTN	83.4 ± 14.3	60.4–97.3	25 ppm $FeCl_3$	75.8 ± 11.0	57.3–92.4	25 ppm $Al_2(SO_4)_3$
HHCB	79.2 ± 9.9	60.0–91.0	25 ppm $FeCl_3$	76.4 ± 5.5	64.8–84.6	25 ppm $Al_2(SO_4)_3$
ADBI	77.7 ± 16.8	49.6–92.4	25 ppm $FeCl_3$	72.1 ± 11.9	48.2–85.9	25 ppm $Al_2(SO_4)_3$
DCF	21.6 ± 19.4	−0.5 to 46.5	50 ppm $FeCl_3$	7.3 ± 17.8	−12.7 to 50.8	25 ppm $FeCl_3$
NPX	21.8 ± 10.2	8.9–42.0	25 ppm $FeCl_3$	17.7 ± 16.4	−1.7 to 46.2	Blank
IBP	12.0 ± 4.8	6.7–22.6	25 ppm $FeCl_3$	10.4 ± 8.3	0.2–29.6	Blank
DZP	12.5 ± 18.4	−10.2 to 41.8	25 ppm $Al_2(SO_4)_3$	−9.1 ± 17.9	−37.2 to 35.4	25 ppm $FeCl_3$
CBZ	6.3 ± 15.9	−13.2 to 45.1	Blank	−7.3 ± 11.0	−25.0 to 1.5	25 ppm $FeCl_3$
IPM	7.3 ± 2.4	3.8–11.5	Blank	14.0 ± 15.3	−1.4 to 37.5	25 ppm $FeCl_3$
SMX	6.0 ± 9.5	−7.5 to 18.9	50 ppm $FeCl_3$	0.9 ± 14.4	−13.6 to 21.3	25 ppm $Al_2(SO_4)_3$
ROX	−64.5 ± 35.5	−100 to 0	–	−115 ± 23.3	−148 to −85.9	–
TMP	−32.1 ± 51.1	−134 to 0	–	−37.3 ± 22.7	−58.9 to −4.7	–
ERY	−49.7 ± 27.7	−79 to 0	–	−92.3 ± 15.3	−105 to −73.5	–

2006). Taking into account that real wastewater has been used for this work and that macrolides could be partly enclosed in faeces particles, since they are mainly excreted with the bile and faeces (Gobel et al., 2007), their release during coagulation experiments could justify this behaviour.

Sorption coefficients determined for fragrances from total and soluble concentrations in streams S1 and S2 were: 6970 ± 3350 L/kg, 7270 ± 2050 L/kg and 4800 L/kg for HHCB, AHTN and ADBI, respectively, which were in the range of those reported by Ternes et al. (2004) for primary sludge and Kupper et al. (2006) for raw sludge. Experimentally determined and calculated theoretical removal efficiencies (Eq. (3)) for these substances are plotted in Fig. 3, together with results obtained for DCF. Obtained results indicate that removals exceeded the fraction of PPCPs sorbed onto suspended particles according to their K_d, thus showing that coagulation–flocculation was able to enhance the removal of fragrances and DCF.

Fragrances were removed between 60–91%, 60–97% and 50–92% for HHCB, AHTN and ADBI, respectively (Table 2). The lower removal of the third compound with respect to the other two is

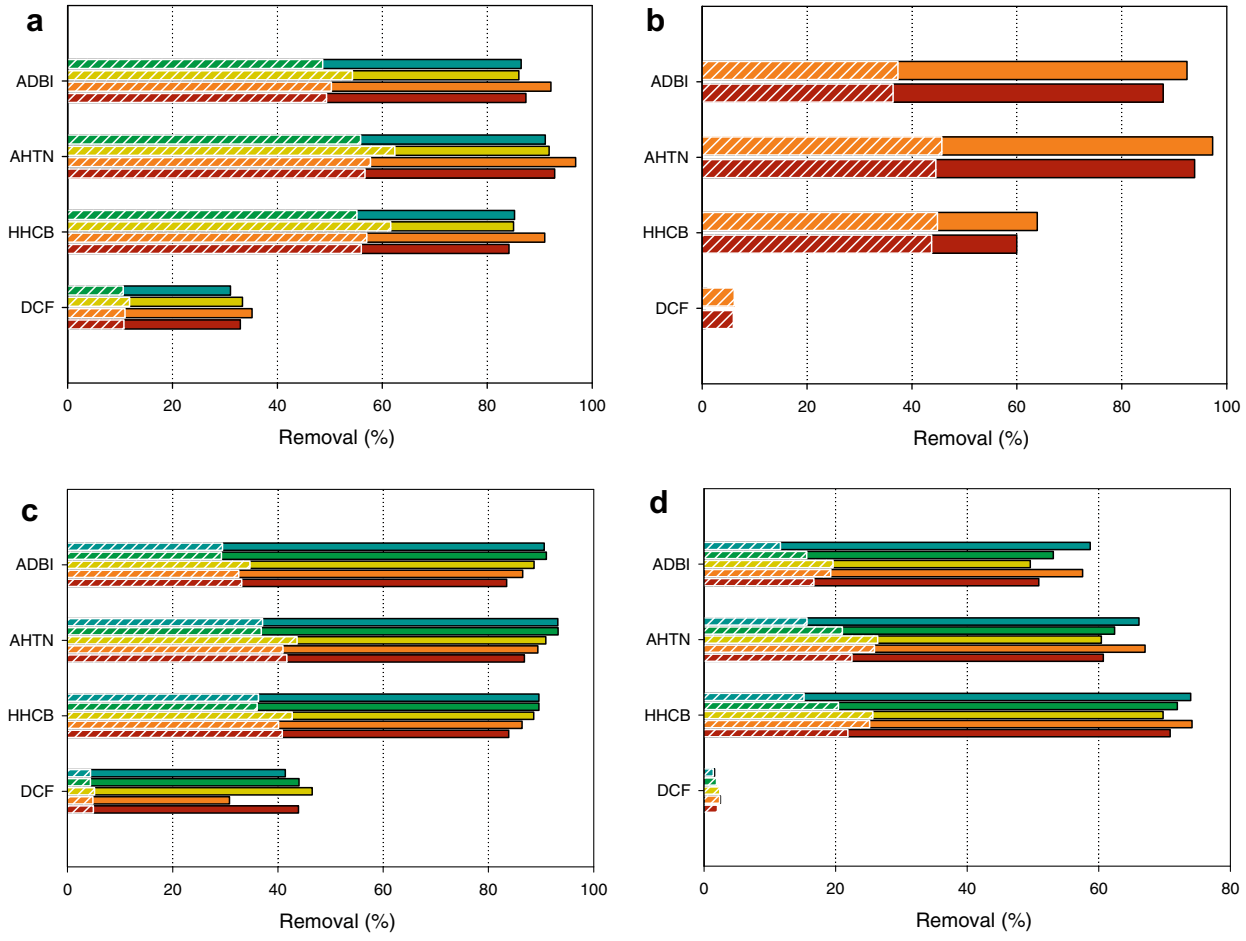

Fig. 3. Removal of fragrances and diclofenac during batch coagulation–flocculation of hospital wastewater: (a) S1; (b) S2 from November 2005; (c) S1; and (d) S2 from March 2006 in the following experiments: blank (■), at 25 ppm (■) and 50 ppm (■) of $FeCl_3$ and at 25 ppm (■) and 50 ppm (■) of $Al_2(SO_4)_3$. Theoretical minimum removal efficiencies according to Eq. (3) are indicated (▨).

concordant with its lower sorption coefficient. The lower limit corresponded generally with the result obtained with stream S2 in March 2006, while the upper limit was achieved with S1 in November 2005 (Fig. 4d and a, respectively). A comparison of the physico-chemical characteristics of these streams showed that the first had the lowest fat content among the four streams (9 mg L^{-1}) whereas the second had the highest (43 mg L^{-1}). Taking into account that fragrances have a strong lipophilic character ($\log K_{ow}$ ~6) and that sorption should be mainly driven by hydrophobic interactions (commonly referred to as absorption), enhanced removal was actually expected in streams with higher fat content. Although only slight differences were observed regarding type of coagulant and doses applied, the use of 25 ppm of $FeCl_3$ led to optimum conditions in most cases. Results determined in the present work at very low concentrations and even without any coagulant addition, were even somewhat higher than those previously determined by Carballa et al. (2005) for primary treatment. During drinking water treatment removal of HHCB has shown to be negligible (Westerhoff et al., 2005; Stackelberg et al., 2007), although the lower fat content of this water source could explain these differences.

Significant removal of diclofenac was only observed for S1, where the initial concentration was reduced by 33.1 ± 1.7% and 41.3 ± 6.1% in the wastewater sampled in November and March, respectively. This pharmaceutical is of acidic nature (pK_a ~4) and therefore mainly deprotonated at circum-neutral pH, thereby adsorption will not occur unless this charge is neutralised. On the other hand, the compound is slightly lipophilic ($\log K_{ow}$ 4.5); consequently it could be absorbed in the lipid fraction of solids. This second characteristic could explain that the removal exclusively occurred in streams S1 whose fat content was higher than in streams S2 (25–43 mg L^{-1} vs. 9–13 mg L^{-1}, respectively). The suitability of coagulation–flocculation processes for removal of DCF was reported by Carballa et al. (2005) for primary treatment of municipal sewage, as well as by Vieno et al. (2006) for drinking water plants, in both cases with higher efficiencies than those measured in the present work (~70%), but also working at higher coagulant doses. On the other hand, Ternes et al. (2002) reported negligible removal of DCF by flocculation using $FeCl_3$ in lab- and full-scale applications at similar doses as those applied in the current experiments. This seems to indicate a correlation between removal efficiencies achieved for DCF and coagulant doses applied in the process, probably related to the establishment of covalent interactions between the deprotonated pharmaceutical and the trivalent cations of coagulants that enhance adsorptive interactions (Carballa et al., 2005).

3.2. Batch flotation experiments

Flotation experiments were conducted with the same wastewater and applying equal conditions as in coagulation–flocculation experiments. Data regarding removal of TSS and COD were summarised in Fig. 4, where a high variability when comparing efficiencies for a specific coagulant type and dose can be clearly observed. Maximum eliminations of TSS were in the range of 60–72%, whereas these upper limits were somewhat lower when focussing on COD, 16–58%, depending on the ratio between solid and soluble organic matter (Mels et al., 2001). In general, flotation led to worse separation of TSS compared to coagulation-flocculation. Results obtained in the present research were comparable to those obtained during pre-treatment of bakery wastewater by Liu and Lien (2001).

Elimination of the considered micropollutants was analysed following an analogous procedure as for coagulation experiments. In a first step removal from the liquid phase for those PPCPs with low sorption potential onto primary sludge was determined (Table 2). The behaviour of antibiotics was similar to what had been observed during coagulation, that is, for macrolides (ROX and ERY) and TMP negative removals were obtained, while SMX concentrations remained almost constant.

Removal of NPX was dependant on the treated stream as can be deduced from the results obtained in 2005 and 2006. In fact, no significant decrease in its initial concentration was detected for S2 in March 2006, whereas 33.0 ± 10.9% and 43.9 ± 3.3 was eliminated during flotation of S1 and S2, respectively, in November 2005. These differences could partially be due to the slightly lower pH of the samples collected in November compared to those from March (7.4–7.9 and 8.5–8.7, respectively), which would led to the presence of a higher fraction of protonated NPX (pK_a 4.2) in the first case that could enhance its interaction with solids, which is

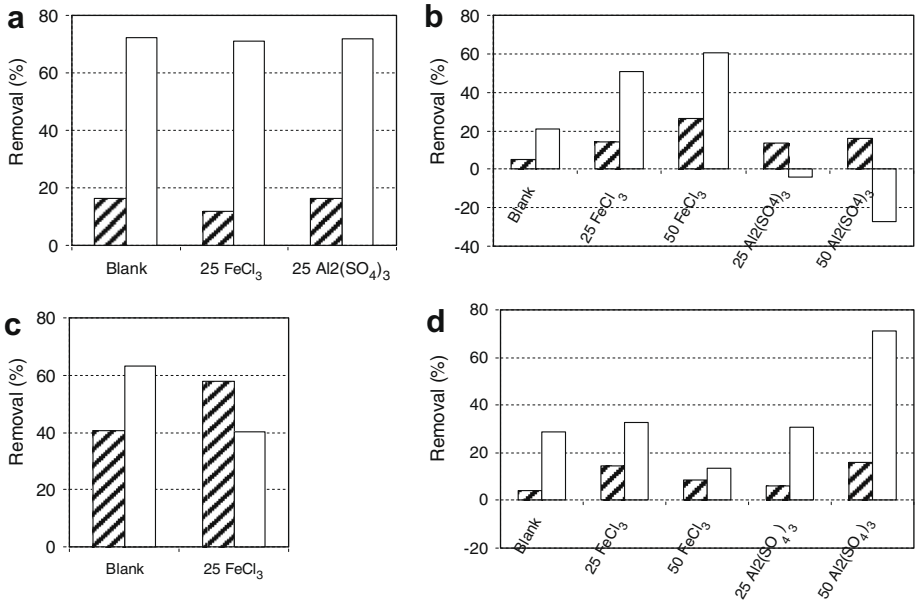

Fig. 4. Removal of total COD (▨) and TSS (□) during flotation of hospital wastewater: (a) S1; (b) S2 from November 2005; (c) S1; and (d) S2 from March 2006.

negligible when the compound is deprotonated. Similar results have been measured for IBP, although the maximum removal observed for this compound was somewhat lower than for NPX (Table 2). These results agree quite satisfactorily with those reported by Carballa et al. (2005).

The anti-epileptic drug CBZ and the tranquiliser DZP were generally not eliminated from the liquid phase, with the exception of S2 in November for which a depletion of 21% and 35%, respectively, were measured, which was indeed somewhat lower than the efficiencies reported by Carballa et al. (2005). In the case of CBZ, whose pK_a is 7, removal could depend on pH which determines the protonation degree of its amide group. In fact, removal was only observed in the sample with the lowest pH, which contains the highest portion of protonated specie which can establish covalent interaction with the negatively charged surface of solids (adsorption).

The fate of fragrances and DCF was analysed on the basis of total concentrations of the compounds (Eq. (2)) and compared with the minimum removal efficiency expected according to separation of TSS and sorption coefficients of these compounds (Eq. (3)). The corresponding results are shown in Fig. 5. As occurred in the coagulation assays, removal of fragrances and DCF was significantly higher than expected on the basis of TSS separation, even in the absence of external flotation additives. Removal of DCF was only observed when wastewater collected in November was subject to flotation, at efficiencies in the range of 13–51%, very close to the removal of 20–45% previously reported by Carballa et al. (2005) for this type of treatment. Surprisingly, the highest efficiency of flotation was achieved with the sample of S2 collected in November (Fig. 5b) which does not correspond to the sample with the highest amount of fat as occurred during coagulation, but with the most acidic one. Removal efficiency seemed to be dependant on the state of the acid-base equilibrium of this acidic compound.

As expected beforehand, highest efficiencies with flotation were measured for the most lipophilic compounds, namely fragrances. Removals of 65–85%, 57–92% and 48–86% were obtained for HHCB, AHTN and ADBI, respectively (Table 2), being these upper limits slightly lower than those achieved by coagulation. Generally, the use of coagulants improved the process, offering the aluminium based reagent better results than the ferric one. As occurred in coagulation experiments, the degree of musk separation correlated with the fat content of the wastewater used, which confirms that the process is mainly driven by absorption, as had been already postulated by Carballa et al. (2005).

3.3. Continuous experiments

The hospital effluent was first continuously treated in the coagulation-flocculation pilot plant at three different conditions: (i) without external additions (blank); (ii) using 25 mg L^{-1} of $Al_2(SO_4)_3$ as coagulant; and (iii) in the presence of 25 mg L^{-1} of $FeCl_3$. The selection of these operational conditions was based on the results obtained during batch experiments, which indicated that working at the higher coagulant dose of 50 mg L^{-1} did not lead

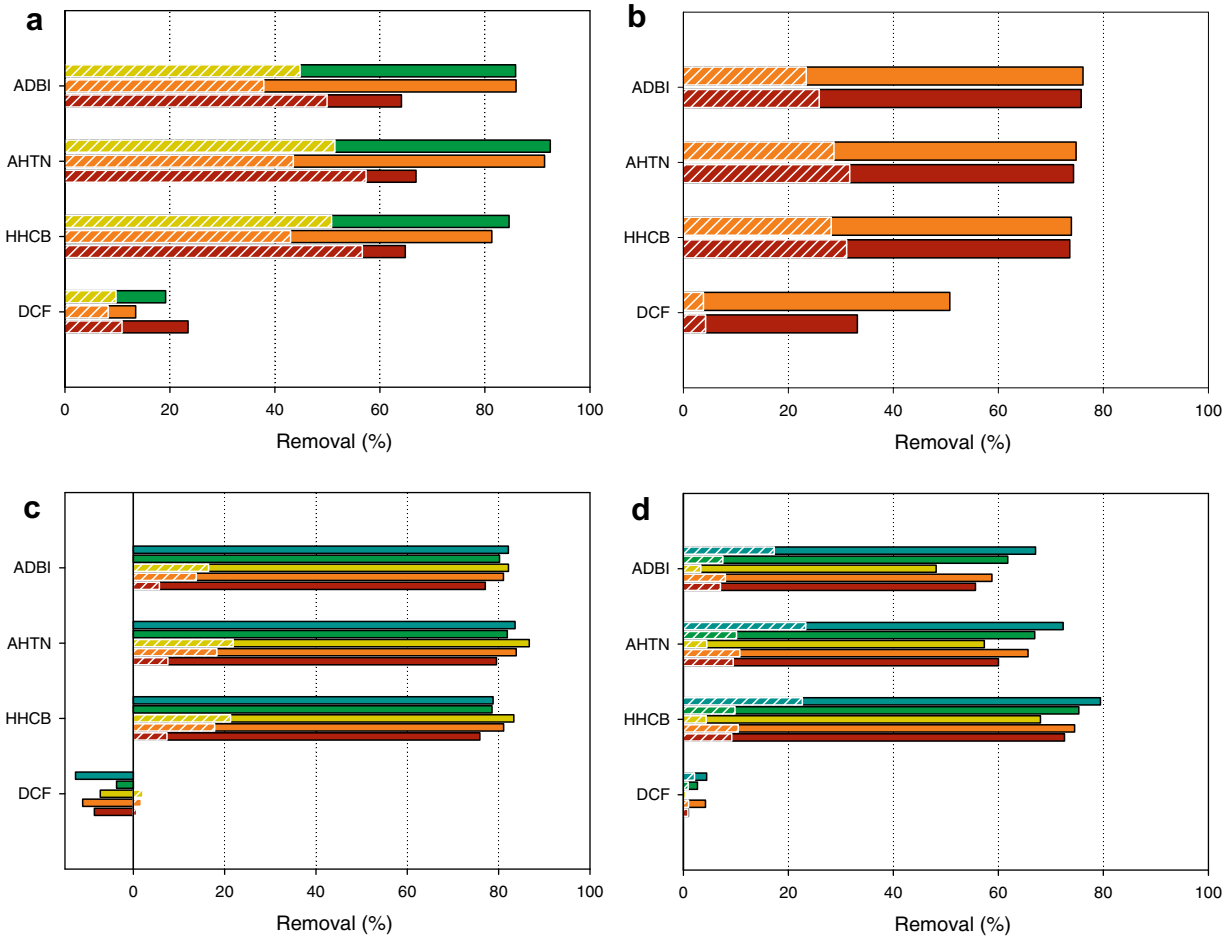

Fig. 5. Removal of fragrances and diclofenac during flotation of hospital wastewater: (a) S1; (b) S2 from November 2005; (c) S1; and (d) S2 from March 2006 in the following experiments: blank (■), at 25 ppm (■) and 50 ppm (■) of $FeCl_3$ and at 25 ppm (■) and 50 ppm (■) of $Al_2(SO_4)_3$. Theoretical minimum removal efficiencies according to Eq. (3) are indicated (▨).

to an improvement in the removal efficiency of PPCPs. The effluents of the pilot plant were afterwards treated in the batch flotation cell in order to evaluate the resulting enhancement of the pre-treatment efficiency. Results regarding removal of conventional wastewater parameters during coagulation–flocculation were 88 ± 3% and 78 ± 10% for TSS and 52 ± 5% and 30 ± 14% for COD during the first and the second experiment, respectively. After flotation removals of TSS and COD were increased in 4 ± 3% and 4 ± 2%, respectively, in experiment I and in 14 ± 8% and 7 ± 4%, respectively, in experiment II. As observed in batch experiments, removal of COD was dependant on the fraction of total COD attributable to solid particles (62% and 39% in wastewaters from the first and second experiment, respectively). It is worth to point out that, despite the high TSS concentration of the wastewater collected for the first experiment (1562 mg TSS L^{-1}), removal of TSS was still very high (88 ± 3%) considering the low coagulant doses applied compared to other works (Jain et al., 2001). The mean TSS removal efficiency of the combined coagulation–flotation process was 92% for both experiments (92 ± 1% and 92 ± 5% for operation I and II, respectively), although in the first the contribution of flotation was almost negligible, whereas in the second the slightly lower performance of the coagulation-flocculation step was compensated by better results during flotation. Although the process was very efficient without any coagulant addition, somewhat better results were achieved in the presence of aluminium salts. In general, these results are in good agreement with those obtained during batch treatment.

Occurrence of the considered PPCPs during the combined coagulation–flotation process is presented in Fig. 6. In the case of antibiotics and iopromide, only data about the performance of coagulation during the second experiment were available, whereas for the rest of compounds a complete analysis was performed. Results obtained during both experiments were very well reproduced and are in concordance with the main conclusions drawn from previous batch analyses.

The compounds which were not affected by the treatment were IPM, NPX, CBZ and DZP, as previously observed in batch experiments for all substances except for NPX for which maximum removals of 42% and 46% were measured during coagulation and flotation processes, respectively. The shorter settling time available in the continuous plant compared to batch systems (20 vs. 60 min) could be responsible for the worse efficiencies obtained in the first.

On the other hand, when $Al_2(SO_4)_3$ was added as coagulant, slight removal of IBP was observed during both experiments (33–39%) in the coagulation-flocculation pilot plant, while flotation was not effective in increasing this removal. These results were somewhat better than those obtained in the Jar-Test experiments (Table 2).

As it was concluded from batch assays, fragrances and to a lesser extent DCF were the most efficiently removed compounds from the considered PPCPs. Maximum elimination of DCF was 53% and 60% for the first and the second experiment, respectively, achieved when working with 25 mg L^{-1} of $Al_2(SO_4)_3$. Mean removal efficiency for fragrances in experiment I were 93.3 ± 1.0%, 95.4 ± 0.9% and 92.5 ± 0.4% for HHCB, AHTN and ADBI, respectively, indicating that the performance of the process was independent on operation conditions. This was a result of the balance between coagulation and flotation, that is, when coagulation was less efficient, it was compensated by higher efficiencies during flotation (Fig. 6 I). While the maximum removals attained were very similar in both assays, it was only achieved when using the aluminium coagulant in the second experiment (Fig. 6 II), being the maximum efficiencies attained 91.3%, 90.1% and 86% for HHCB, AHTN and ADBI, respectively. The suitability of the considered pre-treatment processes for the removal of fragrances was already confirmed in batch experiments, but the continuous mode of operation additionally identified aluminium salts as better coagulants than ferric ones.

As in batch assays, concentrations of antibiotics increased during coagulation–flocculation, even for SMX. For the latter, the

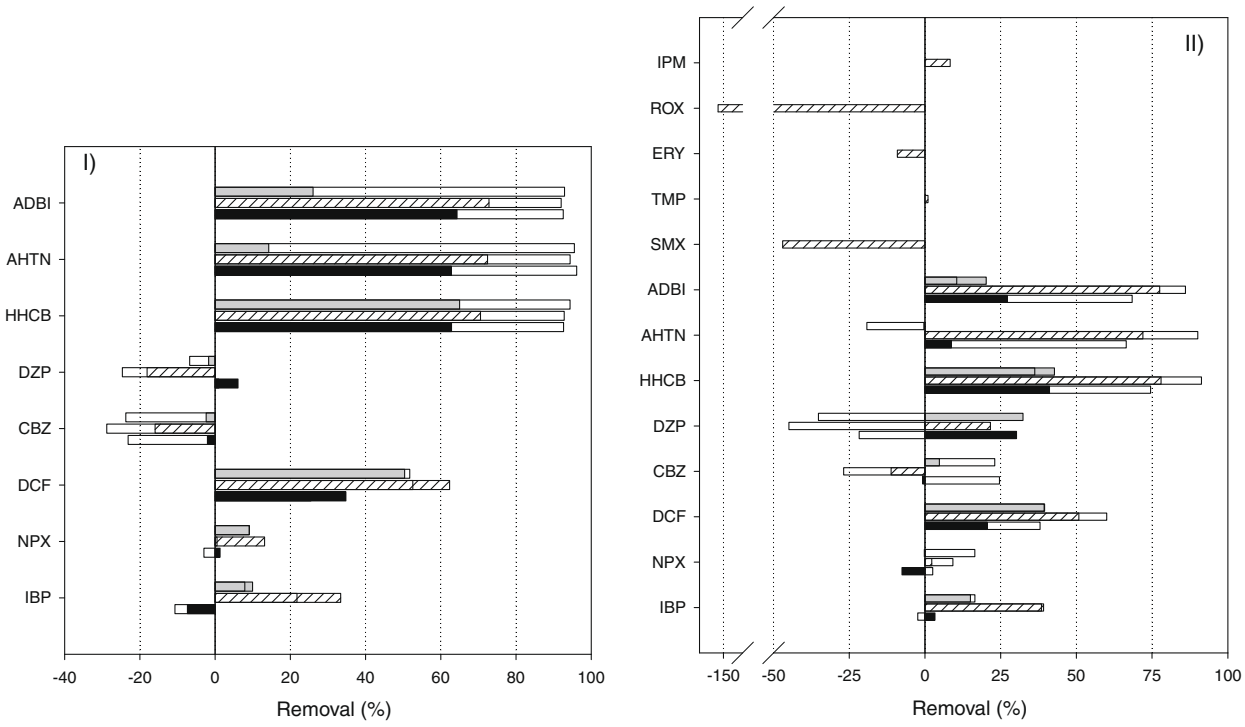

Fig. 6. Removal of PPCPs in the continuous coagulation plant during both experiments (I and II) in the absence of coagulants (■), at 25 ppm of $Al_2(SO_4)_3$ (▨) and at 25 ppm of $FeCl_3$ (▩). Increase in the overall removal when this process was followed by flotation (□).

potential presence in the wastewater of its main metabolite, N^4-acetylsulfamethoxazole (Gobel et al., 2007), that could have been transformed back to its parent compound, might be a possible explanation, although analytical problems seems even more plausible taking into account that after spiking 10 ppb of SMX only 6.6 ppb were detected in the inlet of the pilot plant and 9.7 ppb in its effluent.

4. Conclusions

Coagulation–flocculation can be a suitable pre-treatment option for hospital wastewater in order to partially assimilate their physico-chemical characteristics to that of municipal wastewater. Concentrations of suspended solids, which showed to be up to three fold higher in the hospital effluent considered compared to municipal sewage, could be very efficiently removed during coagulation–flocculation. Similarly, hospital effluents were in some occasion significantly stronger polluted with total COD compared to municipal sewage (up to 3.5 g COD L^{-1}), which was also partially removed during pre-treatment.

Concerning removal of PPCPs, highest efficiencies have been measured for fragrances HHCB, AHTN and ADBI (>90%) which was attributed to their strong lipophilic character that enhanced their removal by absorption. This explains also the fact that better results were obtained in streams with higher fat content. For IBP, NPX and DCF the maximum decrease in concentration was in the range of 30–60%, according to their lower lipophilicity. The compounds IPM, CBZ, DZP and antibiotics were in general not eliminated from the liquid phase.

The main outcome of the present work is that the proposed pre-treatment strategy for hospital effluents has two main advantages: (i) the content of suspended solids and total COD in these streams can be significantly reduced and thus assimilated to that of municipal wastewater; and (ii) lipophilic compounds, such as fragrances, are removed to a high extent before entering municipal STPs, thus avoiding their accumulation on primary and secondary sludge. It is more feasible to treat the relatively small amount of sludge generated during pre-treatment of a small but more concentrated stream than the whole amount of excess sludge generated in conventional STPs.

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