Removal of trace organic pollutants and removal mechanisms using catalyst-immobilized resin/ultrafiltration hybrid system

S. Kim, J. H. Kim, T. B. Yoon, C. H. Lee, H. H. Kwon and D. J. Lim

ABSTRACT

A homogeneous catalyst, iron-tetrasulfophthalocyanine (FeTsPc), was electrostatically immobilized on the powdered anion exchange resin (Amb-FeTsPc) for the enhanced removal of selected pharmaceuticals and endocrine disrupting chemicals (EDC) (cefaclor, diclofenac, ibuprofen and bisphenol-A). It removed $40 \sim 99\%$ of four target pollutants. Moreover, the removal efficiencies were augmented to $>99\%$ in combination with hydrogen peroxide owing to the oxidation of pollutants via activated FeTsPc. The effect of pH on the removal efficiency was investigated in relation to the physicochemical properties, such as hydrophilicity, electric charge and oxidability, of target pollutants. The Amb-FeTsPc/ultrafiltration hybrid system showed high removal efficiencies for target compounds with negative charge and/or high oxidability (bisphenol-A: $\sim 90\%$, cefaclor: $\sim 100\%$, diclofenac: $\sim 100\%$) but relatively low removal efficiency for target compounds with low oxidability (ibuprofen: $\sim 60\%$) for 8 h of operation time. The removal mechanisms for all four compounds by Amb-FeTsPc were also investigated in terms of adsorption, ion exchange and oxidability.

Key words | Amberlite, endocrine disrupting chemicals, hybrid system, iron-tetrasulfophthalocyanine, pharmaceuticals, ultrafiltration

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INTRODUCTION

Pharmaceuticals which have been widely used in human and veterinary medicine for disease control pose a threat to aquatic life and possibly to people. Massive amounts of discarded pharmaceuticals are flushed down the drain and then detected in drinking water sources (Stan *et al.* 1994; Buser *et al.* 1998; Kumerer *et al.* 1998; Xia *et al.* 2005; AWWA 2007; Kim *et al.* 2007; Larsson *et al.* 2007; Santos *et al.* 2007). In addition, as the plastic and polymer resin industries have rapidly expanded to meet increasing demands, chemicals categorized as endocrine disrupting chemicals (EDCs) have been released into the aquatic environment (AWWA 2007; Kim *et al.* 2007). Recent studies have revealed that some of these chemicals, even in small amounts, are extremely harmful to human health and to

other organisms (Carey & Bryant 1995; Facemire *et al.* 1995; Hess *et al.* 1997; Solomon & Schettler 2000; Ottinger *et al.* 2002).

Although EDCs/pharmaceuticals are continuously being released into the environment by humans and/or animals, the removal efficiency of these emerging trace organic pollutants by conventional water/wastewater treatment processes such as coagulation/flocculation, adsorption and chlorination has not been shown to be effective, especially for the removal of hydrophilic and/or neutral molecules (Adams *et al.* 2002; Ternes *et al.* 2002; Deborde *et al.* 2004; Lee *et al.* 2004; Westerhoff *et al.* 2005; Snyder *et al.* 2007). In an attempt to improve this situation, several advanced treatment methods for the removal of EDCs and

pharmaceuticals have been reported, including electro-chemical oxidation, ozonation and photo-catalytic oxidation. Unfortunately, however, these treatment methods also require high investment and/or operating costs (Boscoletto *et al.* 1994; Acero *et al.* 2000; Fukahori *et al.* 2003; Gozmen *et al.* 2003; Huber *et al.* 2003; Kaneco *et al.* 2004; Zhou *et al.* 2004; Snyder *et al.* 2006).

To address these issues, homogeneous metallo-tetra-sulfophthalocyanine (MeTsPc) and its heterogeneous forms, known to be a catalyst for the oxidation of phenolic species in the presence of oxidants such as hydrogen peroxide, has been the subject of growing attention because of its high reactivity and because no additional energy consumption is required (Sorokin & Meunier 1994; Sorokin *et al.* 1995, 2002; Sorokin & Tuel 2000; Grootboom & Nyokong 2002; Hu *et al.* 2004; Agboola *et al.* 2005). In our previous study, we identified the effectiveness of homogeneous/heterogeneous iron(III)-tetrasulfophthalocyanine (FeTsPc) for the removal of selected EDCs and/or pharmaceuticals and hybridized

it using nanofiltration (NF) in order to remove the concentrated pollutants in the retentate of NF (Kim *et al.* 2008a,b, 2009).

In this study, it was attempted to hybridize heterogeneous FeTsPc using an ultrafiltration (UF) system. To the best of our knowledge, no work has been done on applying this catalyst to a continuous UF system although some researchers have tried to hybridize UF systems with adsorbents (e.g. powdered activated carbon) or catalysts (e.g. titanium dioxide), which could remove organic pollutants either physically or chemically (Molinari *et al.* 2008; Lee *et al.* 2009; Jia *et al.* 2009).

First, FeTsPc was electrostatically immobilized on the powdered anion exchange resin–Amberlite (Amb)–to prepare a catalytic adsorbent (Amb-FeTsPc) for the removal of selected EDCs and pharmaceuticals (Figure 1). The effect of the pH conditions on the removal mechanisms and removal efficiencies was evaluated in a batch test with regard to physicochemical properties of individual target pollutants
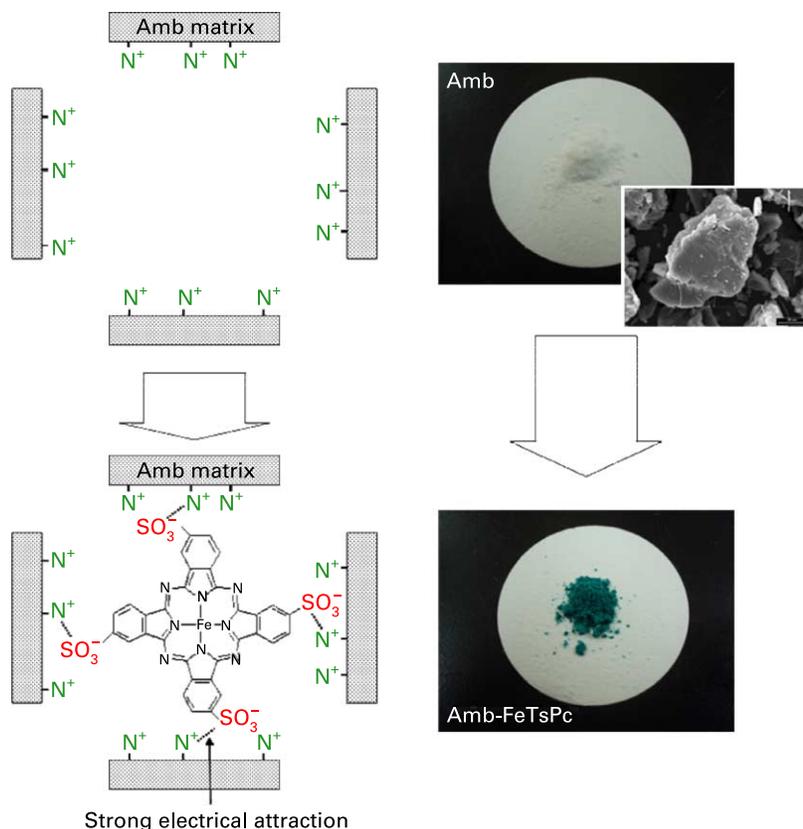

Figure 1 | Schematic diagrams and images of FeTsPc immobilization onto the Amberlite.

(e.g. hydrophilicity, electrical charge and oxidability). Then the UF process was hybridized with Amb-FeTsPc for the effective separation of Amb-FeTsPc from the solution. Finally, the removal mechanisms and removal efficiencies for the target pollutants by the UF-hybrid system were compared with those of the batch tests.

MATERIALS AND METHODS

Materials

FeTsPc, bisphenol-A (BPA, lot#: 239658), cefaclor (lot#: C6895), diclofenac (lot#: D6899), ibuprofen (lot#: I1892), hydrogen peroxide (H_2O_2, 35 wt%), phosphate buffer solution and methanol were purchased from Aldrich (USA) and used without further purification. A stock solution of each solute ($100 \, mg \, l^{-1}$) was prepared by dissolving each solute in DI water prior to performing all of the experiments. Amberlite IRA-400 (Amb) was also purchased from Aldrich (USA) and used after washing in a mixed solution (methanol: DI water = 1:1) for more than 1 day. Then it was ground and sieved by 200×325 mesh sieve. The physicochemical properties and molecular structures of target pollutants and FeTsPc are summarized in Table 1.

A hollow fibre UF membrane (ZeeWeed 500C, ZENON, Canada), which is made of polyvinylidene fluoride (PVDF), was used for the continuous UF experiments. The pore size and the effective membrane area are $0.04 \, \mu m$ and $83.5 \, cm^2$, respectively.

Immobilization procedure

The immobilization procedure was performed as follows: 30 mg of FeTsPc was dissolved in the mixed solution of methanol and DI water at a volume ratio of 1:1 (200 ml total). Then, 1 g of the powdered-Amberlite was added into the FeTsPc solution and gently stirred in the dark at room temperature for 24 h. The resulting blue-coloured powder–FeTsPc-immobilized powdered Amberlite (Amb-FeTsPc, in this article)–was obtained by separating it from the solution by centrifugation. Then, Amb-FeTsPc was dried in the oven at 60°C for more than 24 h and stored in the vial for the next use. The fraction of FeTsPc immobilized on Amberlite, defined by the mass ratio of immobilized FeTsPc to Amberlite, was determined by measuring the residual FeTsPc concentration in the solution after the immobilization procedure with UV-VIS spectroscopy (DR-4000, HACH, USA). It is worth noting that the mass fraction of FeTsPc immobilized on Amberlite of the powdered Amb-FeTsPc is much higher (2.9 wt%) than that of the bead-type Amb-FeTsPc (0.9 wt%) (Kim et al. 2009).

Catalytic oxidation of target pollutants via homogeneous FeTsPc with H_2O_2

The amounts of 2.5 mg of FeTsPc and 0.5 ml of each target pollutant (from the $100 \, mg \, l^{-1}$ stock solution) were added to the methanol/DI water mixture (1:1 vol%) to a final volume of 50 ml. Then the mixture was distributed between five glass vials each with a volume of 10 ml. The oxidation reaction started immediately after injecting the desired volume of H_2O_2 (3.5%) into the solutions by a micropipette. After 30 min of reaction time, 1 ml of sample was taken from each vial and the concentration of pollutants was measured using high performance liquid chromatography (HPLC).

Removal of target pollutants via Amb-FeTsPc with/without H_2O_2

Target pollutant solutions ($1 \, mg \, l^{-1}$, 200 ml) were prepared by adding 2 ml of stock solutions ($100 \, mg \, l^{-1}$) to 195 ml of DI water and stirring vigorously with a magnetic bar. Then, appropriate amounts of 1 M HCl, 0.1 M NaOH or phosphate buffer solution were added to the solutions in order to adjust them to the desired pH. After this, 40 mg of Amb-FeTsPc was added to the solution, and then ~2 ml of samples were taken from the solution at certain time intervals. If required, 0.1 ml of H_2O_2 (3.5%) was injected into the solution just after the addition of Amb-FeTsPc. The concentration of pollutant in the samples was quantified using HPLC after $0.45 \, \mu m$ filtration for the removal of Amb-FeTsPc particles from the solution.
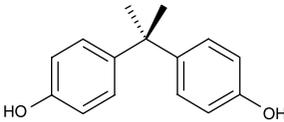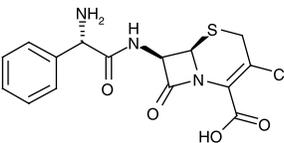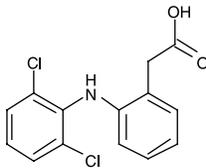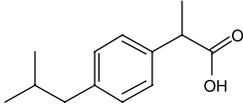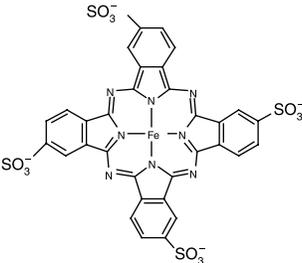
Amb-FeTsPc/UF hybrid system

A schematic depiction of the continuous Amb-FeTsPc/UF membrane system is given in Figure 2 and operating

conditions are summarized in Table 2. The submerged-type UF membrane was located in the centre of the reactor and suction was performed at a constant flux ($72 \, l \, m^{-2} \, h^{-1}$) using a peristaltic pump. The feed solution in the external reservoir ($0.1 \, mg \, l^{-1}$ of target pollutant) was continuously fed into the reactor at a constant flow rate of permeate in order to maintain constant reactor volume (1.2 l). H_2O_2 solution was also continuously fed into the reactor at $0.3 \, ml \, h^{-1}$ using a syringe pump. At startup, the reactor contained $0.1 \, mg \, l^{-1}$ (the same concentration as in the external pollutant reservoir) of target pollutant. Just after the addition of Amb-FeTsPc (120 mg) to the reactor, the filtration started. The permeate flux and transmembrane pressure (TMP) were monitored using a computer connected to an electronic balance and a pressure sensor, respectively. Backwashing, if needed, was performed for 1.2 min every 2 h using the permeate in order to detach the adsorbed Amb-FeTsPc on the membrane surface.

Table 1 | Physicochemical properties of target compounds and catalyst

| Compound	Classification	Molecular structure	Molecular weight (Da)	Log K_{ow}	pKa
Bisphenol-A (BPA)	EDCs		228	3.3	$pKa_1 = 9.6$ $pKa_2 = 10.2$
Cefaclor	PhACs (antibiotic)		368	< 1	$pKa_1 = 2.4$ $pKa_2 = 7.2$
Diclofenac	PhACs (non-steroidal anti-inflammatory drug)		296	0.7	4.2
Ibuprofen	PhACs (non-steroidal anti-inflammatory drug)		228	3.9	4.9
Iron(III)-tetrasulfophthalocyanine (FeTsPc)	Photo-sensitizer, homogeneous catalyst		978	–	~2
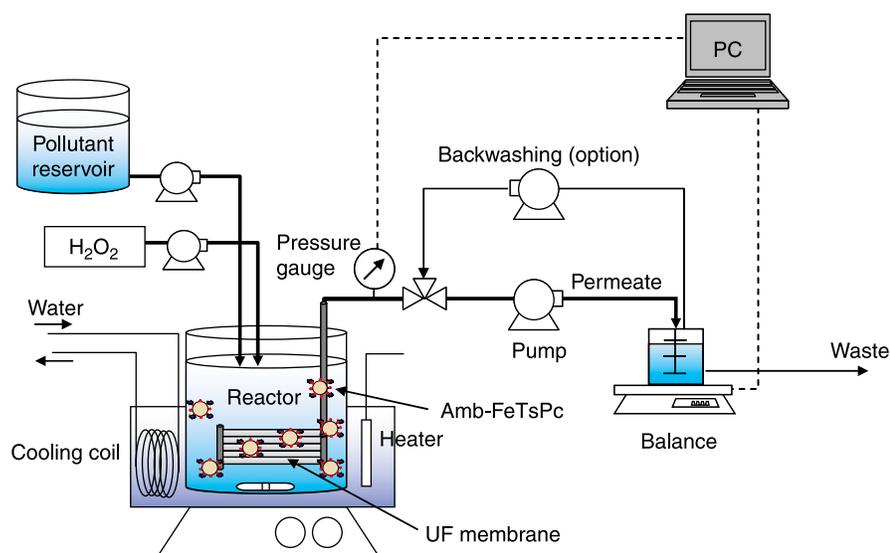
Figure 2 | Schematic diagram of the Amb-FeTsPc/UF system.

Analytical methods

The concentration of target compound was quantified using HPLC: a 250 mm × 4.6 mm, OPTIMAPAK C18 column connected to UV detector (2487 dual λ absorbance detector, Waters, USA). The mobile phase was a mixture of water/acetonitrile (50/50, v/v, 0.1 vol% phosphoric acid for BPA, diclofenac and ibuprofen and 85/15, v/v, 0.1 vol% phosphoric acid for cefaclor) pumped at a flow rate of 1 ml min^{-1}. The detection wavelength was set at 228 nm for BPA, diclofenac and ibuprofen, and at 260 nm for cefaclor.

The surface of the UF membrane was observed using a scanning electron microscope (JSM 5410LV, JEOL, Japan).

Table 2 | Operating conditions of Amb-FeTsPc/UF hybrid system

Feed concentration of pollutants	0.1 mg l^{-1}
Initial concentration of Amb-FeTsPc	100 mg l^{-1}
Reactor volume	1.2 l
Membrane area	83.5 cm^2
Flux	72 l m^{-2} h^{-1}
HRT	2 h
H$_2$O$_2$ feeding rate	0.3 ml h^{-1}
pH (by phosphate buffer)	7.2
Mixing intensity	63.6 s^{-1}
Temperature	25°C
Backwashing interval	1.2 min/2 h

RESULTS AND DISCUSSION

Removal of target pollutants via homogeneous FeTsPc with H$_2$O$_2$

The oxidability of individual target pollutants via homogeneous FeTsPc/H$_2$O$_2$ was examined for different dosages of H$_2$O$_2$ in the presence of organic co-solvent (methanol) prior to investigating the removal efficiency of target pollutants via Amb-FeTsPc/H$_2$O$_2$. As shown in Figure 3, BPA and diclofenac were almost completely degraded via homogeneous FeTsPc/H$_2$O$_2$, even in a low H$_2$O$_2$ concentration (~ 1.7 mM). On the other hand, only $\sim 30\%$ of cefaclor was degraded via homogeneous FeTsPc/H$_2$O$_2$ with the same amount of H$_2$O$_2$ and the removal efficiency of cefaclor stabilized at around 62% even at a higher H$_2$O$_2$ concentration (>6.6 mM). It is likely that rapid deactivation of homogeneous FeTsPc at a high H$_2$O$_2$ concentration would limit further removal of cefaclor (d'Alessandro *et al.* 2003a,b). Ibuprofen was hardly removed via homogeneous FeTsPc/H$_2$O$_2$ even at the highest H$_2$O$_2$ concentration (12.1 mM). The degradation of organic compounds by FeTsPc/H$_2$O$_2$ is known to be initiated by the attack of the activated FeTsPc on the electron-deficient carbon–generally, the carbon in the aromatic ring–which is bound to the electronegative functional groups (e.g. —OH, =O, —Cl) (Sorokin *et al.* 1996; Rajendiran & Santhanalakshmi 2006).
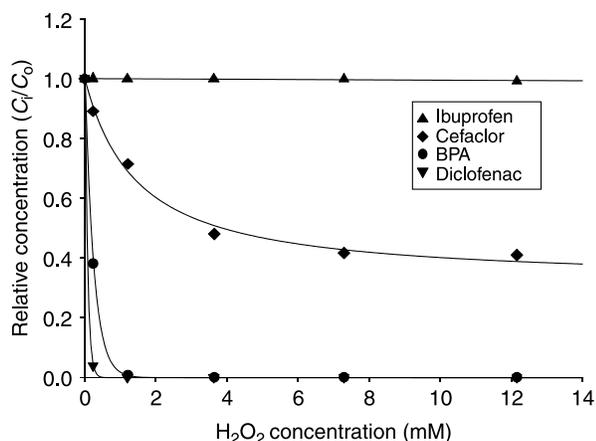
Figure 3 | Effect of H_2O_2 concentration on oxidation of target pollutants via homogeneous FeTsPc/H_2O_2 (C_0 = 1 mg l^{-1}, [FeTsPc]$_{homogeneous}$ = 50 mg l^{-1}, volume = 10 ml (methanol:DI water = 1:1 vol%), pH = 7.2).

Therefore, unlike the other compounds, the aromatic ring of ibuprofen would be much more stable to the oxidation because it has no functional groups directly bound to the aromatic ring. From these results, the oxidability of target pollutants via homogeneous FeTsPc/H_2O_2 can be ordered as follows: diclofenac > BPA > cefaclor > ibuprofen.

Effect of pH on the overall removal efficiency via Amb-FeTsPc without H_2O_2

Since Amberlite is an anion exchange resin with quaternary ammonium group ($-R_4N^+$) on the hydrophobic matrix (styrene-divinylbenzene), Amb-FeTsPc could also remove micro-organic pollutants via an ion exchanging mechanism and/or adsorption even in the absence of H_2O_2 (Carmona et al. 2006; Kim et al. 2009). Therefore, the overall removal efficiencies of the target pollutants via Amb-FeTsPc were evaluated under different pH conditions in order to assess the major removal mechanism of Amb-FeTsPc in the absence of H_2O_2 (Figure 4).

Seventy per cent and ~99% of BPA were removed by Amb-FeTsPc for 2 h of contact time at pH 7.2 and 10.3, respectively. Considering that the pKa$_1$ and pKa$_2$ of BPA are 9.6 and 10.2, respectively, most of the BPA should be unionized at pH 7.2. In addition, since BPA has hydrophobic characteristics (log K$_{ow}$ ~ 3.32, Table 1), the removal mechanism of BPA at pH 7.2 should be adsorption. On the other hand, at pH 10.3, most of the BPA had a de-protonated form and was readily removed by a fast ion exchanging mechanism.

As shown in Figure 4(b), cefaclor could be hardly removed by Amb-FeTsPc at a pH lower than its pKa$_1$ due to the absence of any ion exchanging removal mechanism as well as its hydrophilic characteristics (Table 1). However, when the pH was increased to 7.2 and 9.0, the removal efficiencies were increased to ~40% and 99% (2 h of contact time), respectively. Since cefaclor is hydrophilic, adsorption could be excluded from the removal mechanisms. Thus, the major removal mechanism for cefaclor can be considered to be ion exchange.

The removal efficiency of diclofenac via Amb-FeTsPc at pH 7.2 was almost 100% (2 h of contact time). Because diclofenac is hydrophilic and negatively charged at pH 7.2, the major removal mechanism would be ion exchange. However, interestingly, more than 82% of diclofenac was removed at pH 2.2 where most of diclofenac is uncharged. Since the K$_{ow}$ value of diclofenac greatly increased with decreasing pH, high removal efficiency of diclofenac at low pH would be caused by adsorption.

The removal rate of ibuprofen via Amb-FeTsPc at pH 7.2 was slightly slower than that of diclofenac but much faster than that of BPA and cefaclor. Like diclofenac, ibuprofen is negatively charged at pH 7.2. Therefore, the rapid decrease of ibuprofen at pH 7.2 should be considered as being mainly due to the fast ion exchanging mechanism. However, the removal efficiency of ibuprofen at pH 2.2 (>20%) was much lower than that that of BPA at pH 7.2 where BPA is also uncharged since ibuprofen has little π–π interaction with Amberlite compared with BPA, even though ibuprofen is slightly more hydrophobic than BPA.

Effect of hydrogen peroxide addition on the overall removal efficiency of target pollutants via Amb-FeTsPc at neutral pH

Figure 5 shows the enhancement of removal efficiency of target pollutants via Amb-FeTsPc in the presence of H_2O_2 at neutral pH. For comparison, the removal efficiency of target pollutants via Amb-FeTsPc without H_2O_2 is also shown in Figure 5. The efficiency of removal of BPA and cefaclor via Amb-FeTsPc with H_2O_2 was greatly enhanced: from 63% to 98% and 40% to 95% in 2 h of reaction time, respectively.
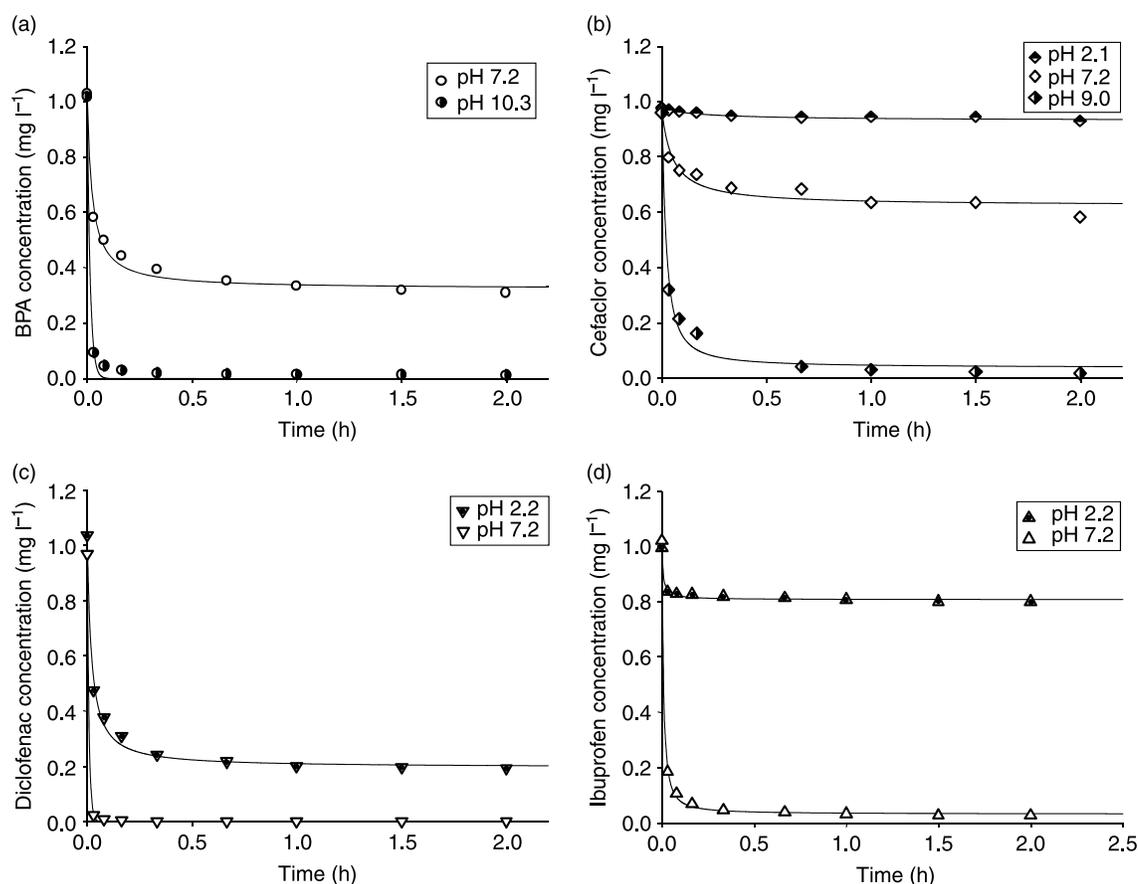
Figure 4 | Effect of pH on the removal rate of the target pollutants via Amb-FeTsPc without H_2O_2: (a) BPA; (b) cefaclor; (c) diclofenac; (d) ibuprofen ([Amb-FeTsPc] = 200 mg l^{-1}, volume = 200 ml).

This is because, in addition to the removal of the pollutants by the adsorption and/or ion exchange mechanism, which are the original properties of Amberlite, the pollutants can be further removed by the oxidation mechanism stimulated by activated FeTsPc in the presence of H_2O_2. On the other hand, the removal of negatively charged pollutants–diclofenac and ibuprofen–did not show significant differences with or without H_2O_2 because the removal by ion exchange was too fast to assess the role of activated FeTsPc.

From these results, it can be concluded that the removal of target pollutants via Amb-FeTsPc was controlled by two different removal mechanisms: first 'sorption' (adsorption and ion exchange) due to the Amberlite itself and, second, 'oxidation' due to the activated FeTsPc in the presence of H_2O_2. Removal efficiency of more than 95% could be achieved for all of the selected target pollutants, which have different physicochemical properties, in a 2 h contact time
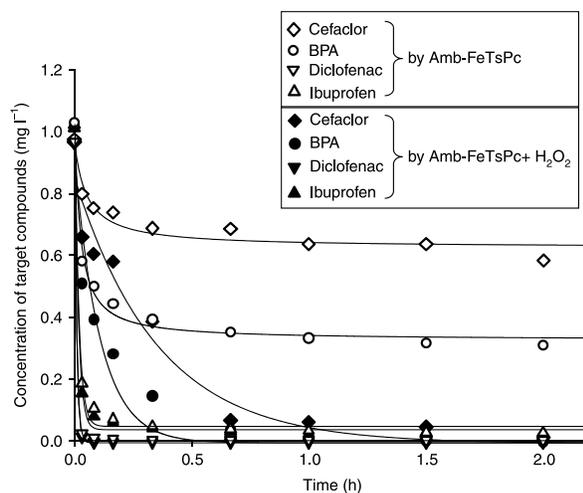

Figure 5 | Effect of addition of H_2O_2 on the overall removal efficiencies of target pollutants via Amb-FeTsPc ([Amb-FeTsPc] = 200 mg l^{-1}, volume = 200 ml, pH = 7.2, [H_2O_2] = 0.61 mM).

by using these two complementary removal mechanisms. Also, it is noteworthy that it is the sorption that mainly affects the overall removal efficiencies because oxidation can take place only after the sorption of target pollutants on to the surface of Amb-FeTsPc.

Continuous Amb-FeTsPc/UF hybrid system

Although Amb-FeTsPc is confirmed as being effective for the removal of selected target pollutants, it is also important to effectively separate and reuse it after the reaction. Moreover, it is essential to examine the applicability of Amb-FeTsPc to a continuous system. Therefore, a hybrid system combining Amb-FeTsPc with UF was devised in order to compare the removal efficiencies of target pollutants with those of a batch experiment.

Effect of Amb-FeTsPc deposition on the membrane surface by the removal of target pollutants

During the operation of the Amb-FeTsPc/UF hybrid system without backwashing, it was observed that the colour of the membrane surface gradually changed from white to light blue, which is the colour of the Amb-FeTsPc. In order to observe the deposition of Amb-FeTsPc onto the UF membrane surface more clearly, the UF membrane was taken out of the reactor after 8 h of operation and analysed
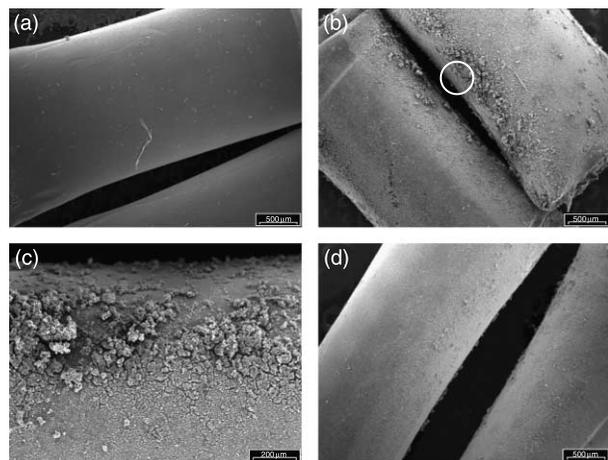
using scanning electron microscopy (SEM). Figure 6 (b) and (c) show that the surface of the UF membrane operated without a backwashing process was covered with massive amounts of Amb-FeTsPc. Because the deposition of Amb-FeTsPc on the membrane surface could possibly result in a reduction of the removal efficiency of pollutants by decreasing the concentration of Amb-FeTsPc in bulk phase, a backwashing process (1.2 min in every 2 h of operation) was introduced to the Amb-FeTsPc/UF hybrid system in order to detach and re-suspend the Amb-FeTsPc deposited on the UF membrane.

As shown in Figure 6(d), it was observed that the backwashing process effectively cleaned out the Amb-FeTsPc deposited on the membrane surface. Moreover, introduction of the backwashing process stimulated the re-suspension of the deposited Amb-FeTsPc particles into the bulk phase and thus, as shown in Figure 7, the removal efficiency of cefaclor was increased in the Amb-FeTsPc/UF hybrid system with backwashing compared with that of the Amb-FeTsPc/UF hybrid system without backwashing.

Effect on membrane performance of Amb-FeTsPc deposition on the membrane surface

Although Amb-FeTsPc was deposited on to the membrane surface in the hybrid system, it was observed that the change in transmembrane pressure (TMP) during 8 h of UF operation was almost negligible ($TMP_{initial} = 14.5$ kPa and $TMP_{8h} = 21.0$ kPa, data not shown) even in the absence of

Figure 6 | Scanning electron microscopic images of various membranes: (a) raw membrane × 5000; (b) membrane operated for 8 h without backwashing × 5000; (c) membrane operated for 8 h without backwashing × 12,500 (point highlighted in (b)); (c) membrane operated for 8 h with backwashing × 5000.
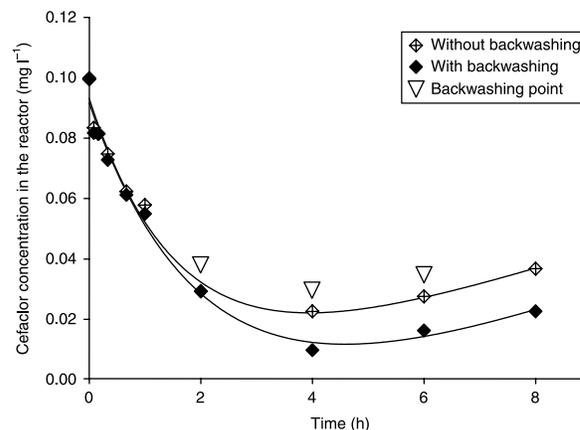

Figure 7 | Comparison of cefaclor concentration in the reactor between Amb-FeTsPc/UF hybrid systems with and without a backwashing process.

the backwashing process. This indicates that deposited Amb-FeTsPc particles would not cause serious membrane fouling or membrane damage.

Removal efficiency of various target pollutants in Amb-FeTsPc/UF hybrid system with backwashing

Figure 8 compares the concentration of target pollutants in the reactor of the Amb-FeTsPc/UF hybrid system with backwashing. In the absence of H_2O_2, BPA was removed only by the adsorption mechanism of Amberlite and the concentration of BPA was decreased to $0.05 \, mg \, l^{-1}$ at the initial time ($<1 \, h$). Then the concentration of BPA gradually increased and reached a peak of $0.08 \, mg \, l^{-1}$ at 8 h of operation due to the attainment of the limit of adsorption capacity of Amberlite. On the other hand,
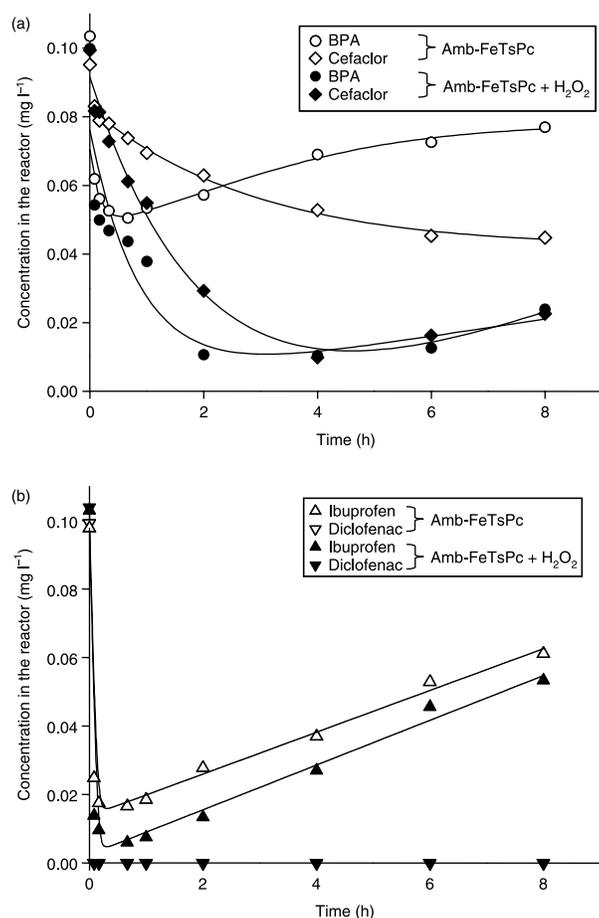

Figure 8 | Variation in target pollutant concentrations in the reactor of the Amb-FeTsPc/UF hybrid system with and without H_2O_2: (a) BPA and cefaclor; (b) ibuprofen and diclofenac.

the concentration of cefaclor, which could hardly be removed by adsorption, decreased more slowly but continuously to $0.045 \, mg \, l^{-1}$ by the end of operation, which indicates that the ion exchanging mechanism is more effective for the removal of negatively charged molecules–even for a slightly charged molecule such as cefaclor–than adsorption in a continuous and long-term experiment. When H_2O_2 was added to the reactor, immobilized FeTsPc was activated by the reaction with H_2O_2 and the oxidation mechanism started being involved in the removal mechanisms. Consequently, both pollutants could be removed more rapidly from the solution and the concentrations decreased to $\sim 0.01 \, mg \, l^{-1}$ at 4 h of operation time. After 4 h of operation, however, it was observed that the concentration of BPA and cefaclor began to increase again due to the limit of oxidation capability. However, these results should be considered in light of the fact that the concentration of pollutants in the external reservoir was set extremely high ($0.1 \, mg \, l^{-1}$) compared with the real aquatic environment (order of $ng \, l^{-1}$) in order to investigate the effect of Amb-FeTsPc hybridization over a short period of time.

The variation of ibuprofen and diclofenac concentration is depicted in Figure 8(b). As explained in the previous section, these negatively charged solutes were readily removed ($>90\%$ removal in 20 min) from the reactor in the hybrid system via the fast ion exchanging mechanism of Amberlite, even in the absence of H_2O_2. Interestingly, however, the concentration of ibuprofen re-increased rapidly and its final concentration was $\sim 0.06 \, mg \, l^{-1}$ even in the presence of H_2O_2 whereas the concentration of diclofenac was maintained below the detection limit of the HPLC during the whole operation time. This is quite a different result compared with that of the batch experiment. This is because ibuprofen can hardly be oxidized by activated FeTsPc and, thus, ion exchange is considered to be the only removal mechanism, even in the presence of H_2O_2, whereas diclofenac can be readily oxidized by activated FeTsPc in addition to the fast ion exchange and strong π—π interaction between the matrix of Amberlite and diclofenac.

In summary, it is likely that adsorption and ion exchange are the dominant removal mechanisms in the initial period of time ($<1 \, h$). After the saturation of sorption capacity, however, the removal of selected pollutants is directly controlled by oxidation capacity via immobilized FeTsPc.

CONCLUSIONS

In this work, a novel ultrafiltration hybrid system combined with Amb-FeTsPc was developed for the effective removal of pharmaceuticals and EDCs, as well as for the efficient separation of Amb-FeTsPc from solution. The removal efficiencies and the removal mechanisms were evaluated using an Amb-FeTsPc hybrid system. Based on the results of this study, the following conclusions can be made:

- The removal of the target pollutants via Amb-FeTsPc is highly affected by pH conditions. In pH conditions higher than the targets' pKa values, rapid ion exchange is the dominant removal mechanism whereas hydrophobic interaction and π—π interaction play an important role under the pH condition lower than the pKa values.

- In the presence of H_2O_2, a dramatic enhancement of removal rate is observed for BPA and cefaclor at neutral pH owing to the oxidation via activated FeTsPc. The sorption (adsorption and ion exchanging) mainly affect the overall removal efficiencies because oxidation can take place only after the sorption of target pollutants onto the surface of Amb-FeTsPc.

- At the initial stage of the hybrid system, negatively charged compounds are rapidly removed by a fast ion exchange mechanism. However, unlike the results from the batch experiment, oxidability of target pollutants plays an important role in the long-term removal. Ibuprofen—negatively charged but with the lowest oxidability of the four compounds—shows the worst removal efficiency at the end of the operation. Adsorption and ion exchange are dominant in the initial removal, and oxidation is dominant in continuous removal in the Amb-FeTsPc/UF hybrid system.

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REFERENCES

Acero, J. L., Stemmler, K. & von Gunten, U. 2000 Degradation kinetics of atrazine and its degradation products with ozone and OH radicals: a predictive tool for drinking water treatment. *Environ. Sci. Technol.* **34**(4), 591–597.

Adams, C., Wang, Y. & Loftin, K. 2002 Removal of antibiotics from surface and distilled water in conventional water treatment processes. *J. Environ. Eng.* **128**(3), 253–260.

Agboola, B., Ozoemena, K. I. & Nyokong, T. 2005 Hydrogen peroxide oxidation of 2-chlorophenol and 2,4,5-trichlorophenol catalyzed by monomeric and aggregated cobalt tetrasulfophthalocyanine. *J. Mol. Catal. A Chem.* **227**(1/2), 209–216.

AWWA Research Foundation 2007 *Endocrine Disruptors and Pharmaceuticals Strategic Initiative Expert Workshop Report*. AWWA Research Foundation, Denver, CO.

Boscoletto, A. B., Gottaridi, F., Milan, L., Pannocchia, P., Tartari, V., Tavan, M., Amadelli, R., De Battisti, A., Barbieri, A., Patracchini, D. & Battaglin, G. 1994 Electrochemical treatment of bisphenol-A containing wastewaters. *J. Appl. Electrochem.* **24**, 1052–1058.

Buser, H. R., Muller, M. D. & Theobald, N. 1998 Occurrence of the pharmaceutical drug clofibric acid and the herbicide mecoprop in various Swiss lakes and in the North Sea. *Environ. Sci. Technol.* **32**(1), 188–192.

Carey, C. & Bryant, C. J. 1995 Possible interrelations among environmental toxicants, amphibian development, and decline of amphibian populations. *Environ. Health Perspect.* **103**, 13–17.

Carmona, M., De Lucas, A., Valverde, J. L., Velasco, B. & Rodriguez, J. F. 2006 Combined adsorption and ion exchange equilibrium of phenol on amberlite IRA-420. *Chem. Eng. J.* **117**, 155.

d'Alessandro, N., Tonucci, L., Bressan, M., Dragani, L. K. & Morvillo, A. 2003*a* Rapid and selective oxidation of metallosulfophthalocyanines prior to their usefulness as precatalysts in oxidation reactions. *Eur. J. Inorg. Chem.* **2003**, 1807–1814.

d'Alessandro, N., Tonucci, L., Dragani, L. K., Morvillo, A. & Bressan, M. 2003*b* Fate of nickel and cobalt sulfophthalocyanines under oxidizing conditions: a spectroscopic investigation. *J. Porphyr. Phthalocya.* **7**, 484–492.

Deborde, M., Rabouan, S. & Gallard, H. 2004 Aqueous chlorination kinetics of some endocrine disruptors. *Environ. Sci. Technol.* **38**(21), 5577–5583.

Facemire, C. F., Gross, T. S. & Guillette, L. J. 1995 Reproductive impairment in the Florida panther: nature or nurture? *Environ. Health Perspect.* **103**, 79–86.

Fukahori, S., Ichiura, H., Kitaoka, T. & Tanaka, H. 2003 Capturing of bisphenol-A photodecomposition intermediates by composite TiO_2-zeolite sheets. *Appl. Catal. B* **46**, 453–462.

Gozmen, B., Oturan, M. A., Oturan, N. & Erbatur, O. 2003 Indirect electrochemical treatment of bisphenol-A in water via electrochemically generated fenton's reagent. *Environ. Sci. Technol.* **37**, 3716–3723.

Grootboom, N. & Nyokong, T. 2002 Iron perchlorophthalocyanine and tetrasulfophthalocyanine catalyzed oxidation of

cyclohexane using hydrogen peroxide, chloroperoxybenzoic acid and tert-butylhydroperoxide as oxidants. *J. Mol. Catal. A Chem.* **179**(1/2), 113–123.

Hess, R. A., Bunick, D. & Lee, K. H. 1997 A role for oestrogens in the male reproductive system. *Nature* **390**(6659), 509–512.

Hu, M., Xu, Y. & Zhao, J. 2004 Efficient photosensitized degradation of 4-chlorophenol over immobilized aluminum tetrasulfophthalocyanine in the presence of hydrogen peroxide. *Langmuir* **20**, 6302–6307.

Huber, M. M., Canonica, S. & Park, G. Y. 2003 Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environ. Sci. Technol.* **37**(5), 1016–1024.

Jia, Y., Wang, R. & Fane, A. G. 2009 Hybrid PAC-submerged membrane system for trace organics removal II: system simulation and application study. *Chem. Eng. J.* **149**, 42–49.

Kaneco, S., Rahman, M. A., Suzuki, T., Katsumata, H. & Ohta, K. 2004 Optimization of solar photocatalytic degradation conditions of bisphenol A in water using titanium dioxide. *J. Photochem. Photobiol. A* **163**, 419–424.

Kim, S. D., Cho, J., Kim, I. S., Vanderford, B. J. & Snyder, S. A. 2007 Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water Res.* **41**, 1013–1021.

Kim, J. H., Kim, S., Lee, C. H., Kwon, H. H. & Lee, S. 2008a A novel nanofiltration hybrid system to control organic micro-pollutants: application of dual functional adsorbent/catalyst. *Desalination* **231**, 276–282.

Kim, J. H., Park, P. K., Lee, C. H., Kwon, H. H. & Lee, S. 2008b A novel hybrid system for the removal of endocrine disrupting chemicals: nanofiltration and homogeneous catalytic oxidation. *J. Memb. Sci.* **312**, 66–75.

Kim, J. H., Kim, S. J., Lee, C. H. & Kwon, H. H. 2009 Removal of toxic organic micro-pollutants with FeTsPc-immobilized Amberlite/H_2O_2: effect of physico-chemical properties of toxic chemicals. *Ind. Eng. Chem. Res.* **48**(3), 1586–1592.

Kumerer, K., Erbe, T., Gartiser, S. & Brinkler, L. 1998 AOX-emissions from hospitals into municipal waste water. *Chemosphere* **36**(11), 2443–2445.

Larsson, D. G. J., de Pedro, C. & Paxeus, N. 2007 Effluent from drug manufactures [sic] contains extremely high level of pharmaceuticals. *J. Hazard. Mater.* **148**, 751–755.

Lee, B. C., Kamata, M. & Akatsuka, Y. 2004 Effects of chlorine on the decrease of estrogenic chemicals. *Water Res.* **38**(3), 733–739.

Lee, S., Lee, J. W., Kim, S., Park, P. K., Kim, J. H. & Lee, C. H. 2009 Removal of 17β-estradiol by powdered activated carbon–Microfiltration hybrid process: the effect of PAC deposition on membrane surface. *J. Memb. Sci.* **326**, 84–91.

Molinari, R., Caruso, A., Argurio, P. & Poerio, T. 2008 Degradation of the drugs Gemfibrozil and Tamoxifen in pressurized and de-pressurized membrane photoreactors using suspended polycrystalline TiO_2 as catalyst. *J. Memb. Sci.* **319**, 54–63.

Ottinger, M. A., Abdelnabi, M. & Quinn, M. 2002 Reproductive consequences of EDCs in birds: what do laboratory effects mean in field species? *Neurotoxicol. Teratol.* **4**(1), 17–28.

Rajendiran, N. & Santhanalakshmi, J. 2006 Metal tetrasulfophthalocyanines catalysed co-oxidation of phenol with 4-aminoanti-pyrine using hydrogen peroxide as oxidant in aqueous micro-heterogeneous system. *J. Mol. Catal. A Chem.* **245**, 185–191.

Santos, J. L., Aparicio, I. & Alonso, E. 2007 Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. A case study: Seville city (Spain). *Environ. Int.* **33**, 596–601.

Snyder, S. A., Wert, E. C. & Rexing, D. J. 2006 Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater. *Ozone Sci. Eng.* **28**(6), 445–460.

Snyder, S. A., Adham, S. & Redding, A. M. 2007 Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination* **202**(1/3), 156–181.

Solomon, G. M. & Schettler, T. 2000 Environment and health: 6. endocrine disruption and potential human health implications. *Can. Med. Assoc. J.* **163**(11), 1471–1476.

Sorokin, A. & Meunier, B. 1994 Efficient H_2O_2 oxidation of chlorinated phenols catalysed by supported iron phthalocyanines. *J. Chem. Soc. Chem. Commun.* **15**, 1799.

Sorokin, A. B. & Tuel, A. 2000 Metallophthalocyanine functionalized silicas: catalysts for the selective oxidation of aromatic compounds. *Catal. Today* **57**(1/2), 45–59.

Sorokin, A., Seris, J. & Meunier, B. 1995 Efficient oxidative dechlorination and aromatic ring cleavage of chlorinated phenols catalyzed by iron sulfophthalocyanine. *Science* **268**, 1163–1165.

Sorokin, A., De Suzzoni-Dezard, S. & Poullain, D. 1996 CO_2 as the ultimate degradation product in the H_2O_2 oxidation of 2,4,6-Trichlorophenol catalyzed by iron tetrasulfophthalocyanine. *J. Am. Chem. Soc.* **118**, 7410–7411.

Sorokin, A. B., Mangematin, S. & Pergrale, C. 2002 Selective oxidation of aromatic compounds with dioxygen and peroxides catalyzed by phthalocyanine supported catalysts. *J. Mol. Catal. A Chem.* **182/183**, 267–281.

Stan, H. J., Heberer, T. & Linkerhagner, M. 1994 Occurrence of clofibric acid in the aquatic system. *Vom Wasser* **83**(5), 57–68.

Ternes, T. A., Meisenheimer, M. & McDowell, D. 2002 Removal of pharmaceuticals during drinking water treatment. *Environ. Sci. Technol.* **36**(17), 3855–3863.

Westerhoff, P., Yoon, Y. & Snyder, S. 2005 Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environ. Sci. Technol.* **39**(17), 6649–6663.

Xia, K., Bhandari, A., Das, K. & Pillar, G. 2005 Occurrence and fate of pharmaceuticals and personal care products (PPCPs) in biosolids. *J. Environ. Qual.* **34**, 91–104.

Zhou, D., Wu, F., Deng, N. & Xiang, W. 2004 Photooxidation of bisphenol A(BPA) in water in the presence of ferric and carboxylate salts. *Water Res.* **38**, 4107–4116.