Removal of Selected Pharmaceuticals from Urine via Fenton Reaction for Agriculture Reuse

Fenton and Fenton-like oxidation treatments have been researched to remove pharmaceutically active compounds from urine.

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Abstract

Pharmaceutically active compounds (PhACs) are excreted by humans mainly with urine and, to a lesser extent, with faeces. This study investigates the effect of Fenton's oxidation on the degradation of three PhACs, namely levofloxacin, ibuprofen and atorvastatin in combination. Therefore, aqueous solution and urine spiked, separately, with the selected PhACs. Fenton and Fenton-like oxidation treatments, namely: H_2O_2 and $FeSO_4$, H_2O_2 and CuCl, and H_2O_2 and Activated Carbon were examined in batch reactors. Results showed that the removal rate ranged from 95 to 99% for PhACs and from 97 to 98% for COD in the aqueous solution. For the artificially contaminated urine, the removal rate ranged from 95 to 99% for PhACs and from 97 to 99% for COD. Biodegradability (BOD_5/COD ratio) improved from 0.09 to 0.7, indicating that the effluent was amenable to biological treatment.

Introduction

Pharmaceutically active compounds (PhACs) have been observed in surface water (Vieno et al., 2007), groundwater (Abdel-Shafy et al., 2008), sewage effluents (Ternes et al., 2004), drinking water and solid waste (Musson and Townsend, 2009). The drug concentrations detected in the environment were generally in the ng/L to µg/L range (Vieno et al., 2007). PhACs can reach the aquatic environment through various sources including pharmaceutical industry, hospital effluents and excretion from humans and livestock (Yanga et al., 2008). PhACs in surface waters is an emerging environmental issue and provides a new challenge to drinking water, wastewater and water reuse treatment systems (Ikehata et al., 2006). Generally, approximately 70% of PhAC forms are excreted with urine (metabolites, conjugates) excreted from human body while 30% with feaces (Lienert et al., 2007). Separate collection and processing of human urine is gaining interest for three important reasons. Firstly, human urine contains the largest fraction of nutrients: nitrogen (80%), phosphorus (50%) and potassium (70%) emitted from households (Vinnerås and Jönsson, 2002). These could be used, after an appropriate treatment if required, as fertilizers in agriculture. Secondly, to reduce the amounts of residual PhACs that are currently discharged through sewer overflows and by wastewater treatment plants (WWTPs) that are not designed to efficiently eliminate these compounds. Thirdly, disconnection of the urine stream (or part of the stream) from the sewer would enable to save energy at WWTPs (Wilsenach and van Loosdrecht, 2006), spent for nitrification of ammonium mainly originating from urine.

Key factors:

- Pharmaceuticals are consumed in high quantities worldwide and the expectations are that these amounts will continue increasing because of improving health care system and longer life expectations of people.
- Approximately 70% of pharmaceuticals are excreted with urine (metabolites, conjugates) from human body while 30% with feaces.
- Fenton's oxidation achieves high removal efficiency of pharmaceuticals from urine, particularly for the non-biodegradable portions, and it is highly dependent on the concentration of oxidant and catalyst.
- Fenton's treatment is rated as uneconomical for treating large volumes of urine. For pre-treatment, lower dose of Fenton's reagents can be used.
- For the elimination of the selected PhACs the tested catalysts (Fe^{2+} or Cu^{1+}) have been more efficient than Activated Carbon

Usage of urine includes the risk of transfer of pharmaceutical residues to agricultural fields. Little is known on the fate of pharmaceuticals regarding their accumulation in soils, transfer to groundwater, and incorporation by plants. The uptake of pharmaceuticals in plants and the effects they exaggerate on plant physiology and development were of major interest when crops are fertilized with urine. Uptake of organic compounds by plants is correlated with their molecular weight (Winker et al., 2008). It is assumed that molecular weight of >1000 (Da) makes the absorption by cellular membranes impossible (Sanderson et al., 2004). Additionally, uptake of pharmaceuticals by plants can affect their growth when dosed in sufficient concentrations (Dolliver et al., 2007).

Treatment of pharmaceutical wastewaters for the removal of PhAC's is a challenging task due to the wide variety of chemicals produced in drug manufacturing plants, which lead to wastewaters of variable compositions (Zwiener and Frimmel, 2000). Likewise, most of the substances related to pharmaceutical industry are resistant to the biological degradation. Therefore, chemical treatments or pre-treatments to increase the effect of biological depuration are necessary. Chemical processes, like Advanced Oxidation Processes (AOPs) have been successfully used for the removal or degradation of recalcitrant pollutants present in wastewater coming from different industries (Klavarioti et al., 2009, Abdel-Shafy et al., 2010). These processes involve the generation of hydroxyl radicals ($HO^{\bullet}$) with high oxidative power. Among AOPs, Fenton´s reagent, has emerged as an interesting alternative for the treatment of dissolved organic pollutants in wastewater streams(Klavarioti et al., 2009). Other examples of AOPs include photo-Fenton and electro-Fenton (Mira et al., 2011).

Fenton Reaction

Under acidic conditions, in the presence of hydrogen peroxide (H_2O_2), Cu^{1+} or Fe^{2+} and organic substrate (RH), the following redox reactions take place:

$$Fe^{2+} \text{ or } Cu^{1+} + H_2O_2 \rightarrow Fe^{3+} \text{ or } Cu^{2+} + HO^- + HO^{\bullet} \quad (1)$$
$$HO^{\bullet} + Fe^{2+} \text{ or } Cu^{1+} \rightarrow Fe^{3+} \text{ or } Cu^{2+} + HO^- \quad (2)$$
$$HO^{\bullet} + RH \rightarrow H_2O + R^{\bullet} \quad (3)$$
$$R^{\bullet} + Fe^{3+} \text{ or } Cu^{2+} \rightarrow R^+ + Fe^{2+} \text{ or } Cu^{1+} \quad (4)$$

Reactions (1) and (2) are initiation and termination reaction, while reactions (3) and (4) are propagation reactions.

Activated carbon (AC) is known to decompose H_2O_2. Presumably, the process involves the exchange of a surface hydroxyl group with a H_2O_2 anion (Reaction 5) The formed surface peroxide is regarded as having an increased oxidation potential which enables the decomposition of another H_2O_2 molecule with release of oxygen (O_2) and regeneration of the AC surface (Reaction 6). Beside this decomposition reaction, H_2O_2 can obviously be activated on the AC surface involving the formation of hydroxyl radicals ($HO^{\bullet}$). AC is considered to function as an electron-transfer catalyst similar to the Haber–Weiss mechanism known from the Fenton reaction, with AC and AC^+ as the oxidized and reduced catalyst states (Reactions 7 and 8). The AC/H_2O_2 process can lead to decay of organic contaminants in aqueous solution (Georgi and Kopinke, 2005).

$$AC–OH + H^+ OOH^- \rightarrow AC– OOH + H_2O \quad (5)$$
$$AC–OOH + H_2O_2 \rightarrow AC– OH + H_2O + O_2 \quad (6)$$
$$AC + H_2O_2 \rightarrow AC^+ + HO^- + HO^{\bullet} \quad (7)$$
$$AC+ + H_2O_2 \rightarrow AC + HO_{2\bullet} + H^+ \quad (8)$$

Afterwards, the hydroxyl radicals are oxidizing the pollutants. The hydroxyl radicals can react according to 4 kinds of reactions with the pollutants:

$$\text{Addition: } HO^{\bullet} + C_6H_6 \rightarrow (OH)\,C_6H_6 \quad (9)$$
$$\text{Hydrogen Abstraction: } HO^{\bullet} + CH_3OH \rightarrow CH_2OH + H_2O \quad (10)$$
$$\text{Electron Transfer: } HO^{\bullet} + [Fe(CN)_4]^{4-} \rightarrow [Fe(CN)_6]^{3-} + HO^- \quad (11)$$
$$\text{Radical Interaction: } HO^{\bullet} + .\,OH \rightarrow H_2O_2 \quad (12)$$

During the Fenton's reaction all the parameters are adjusted to promote the two first reactions (Reactions 9 and 10) between the pollutant and the hydroxyl radicals. The Fenton process usually involves four stages: pH adjustment, oxidation, neutralization, coagulation and precipitation (Geisslinger et al., 1989).

The aim of the present study is to investigate the removal efficiency of selective PhAC's from urine for the purpose of safe urine reuse in agriculture. In this study the laboratory batch investigations were conducted to determine the potential and efficiency of Fenton's oxidation process H_2O_2 and $FeSO_4$, H_2O_2 and CuCl, and H_2O_2 and AC on the degradation of selective PhACs.

Material and Methods

Selected Pharmaceutical Compounds

For a selection of test compounds a number of criteria were taken into account: consumption, occurrence in aquatic environment, differences in physical-chemical properties (e.g. polarity, hydrophobicity) and suspected biological degradability (persistent, biodegradable), potential eco-toxicological effects and availability of analytical methods. The optimum dose was determined according to the maximum removal of both the selected PhACs and chemical oxygen demand (COD) by using of Fenton's oxidation process. Analysis of the selected PhACs samples using UV-Vis spectrophotometer instrument were carried out.

The selected PhAC's were levofloxacine (LEF), ibuprofen (IBP) and atorvastatin (ATV); extra pure (98%) assays were purchased from Merck (Germany). Characteristics of the selected pharmaceutical compounds:

- Atorvastatin (ATV) is a calcium salt under the trade name Lipitor, is a member of the drug class known as statins, used for lowering blood

cholesterol. It also stabilizes plaque and prevents strokes through anti-inflammatory and other mechanisms. The drug has topped the list of best-selling branded in pharmaceutical history, for nearly a decade, since it was approved in 1996, and it exceeds US$125 billion (McCrindle et al., 2003). It is a white to off-white crystalline powder that is insoluble in aqueous solution of pH 4 and below; it is very slightly soluble in water and slightly soluble at pH 7.4 phosphate buffers and acetonitrile, slightly soluble in ethanol and freely soluble in methanol.

- Levofloxacin (LEF) is a synthetic chemotherapeutic antibiotic of the fluoroquinolone drug class and is used to treat severe or life-threatening bacterial infections or bacterial infections that have failed to respond to other antibiotic classes (Nelson et al., 2007). Levofloxacin is associated with a number of serious and life-threatening adverse reactions as well as spontaneous tendon ruptures and irreversible peripheral neuropathy. Chemically, LEF, a chiral fluorinated carboxyquinolone, is the pure (-)-(S)-enantiomer of the racemic drug substance ofloxacin. In solid form, is an odourless, white to yellow, crystallized powder with a melting point of 228.6°C. Its molecular weight is 361. LEF is practically insoluble in water, but is soluble in ethanol and chloroform, and also in ethanol–water mixture,
- Ibuprofen (IBP), from the nomenclature iso-butyl-propanoic-phenolic acid, is a non-steroidal anti-inflammatory drug (NSAID) used for relief of symptoms of arthritis, fever (Van Esch et al., 1995) as an analgesic (pain reliever), especially where there is an inflammatory component, and dysmenorrhea. Ibuprofen is known to have an antiplatelet effect, though it is relatively mild and somewhat short-lived when compared with aspirin or other better-known antiplatelet drugs. Ibuprofen is a ‚core' medicine in the WHO Model List of Essential Medicines, which is a list of minimum medical needs for a basic healthcare system (Su et al., 2003). It is insoluble in water but is soluble in ethanol and acetone. At standard temperature and pressure it is a crystalline solid with a white/off-white colour.

Experimental procedure

Distilled water was artificially contaminated with the selective PhAC's at a concentration of 40 mg/L each (in order to ensure analytical detection limits of UV-Vis spectrophotometer). The experiments were conducted in a jar-test apparatus at room temperature as batch reactors (for each drug separately and/ or in combination). The initial pH of the contaminated water was adjusted to 3 using 0.1 M H_2S0_4. The experiment was started by adding H_2O_2 at variable concentrations to the examined water (to initiate the oxidation reaction) under flash mixing (500 rpm). Furthermore, the catalyst (namely, Fe^{+2}, Cu^{+1}) and / or powdered activated carbon (PAC) was added to the reactors followed by slow mixing (100 rpm). The reaction was allowed to continue for 60 min. Fenton reactions cannot occur at pH > 10. Therefore, the reaction was stopped instantly and thereafter, pH was elevated to more than 10 by adding 1M NaOH under flash mixing for 5 min. at 200 rpm, for the precipitation of iron or copper and the decomposing of residual H_2O_2 before analysis (Talinli and Anderson, 1992). The jar-test was setup for flocculation at 30 rpm for 20 min followed by 60 min for sedimentation.

After determining the optimal dose of H_2O_2 variable concentrations of the catalysts and/or chemicals (namely Fe^{+2}, Cu^{+1} or AC) were added at the pre-determined H_2O_2 dose. Similar experiments were carried out on real urine samples that were artificially contaminated by the selected PhACs in combination.

Artificially Contaminated Urine (ACU) Samples

Urine was collected from urine diversion toilets (Figures 1) implemented in the National Research Centre pilot plant in Cairo, Egypt. None of the toilet users was under any medication with the selective PhACs or any other drugs.

The urine samples were artificially contaminated with an initial concentrations of 40 mg/L for the three selected pharmaceuticals. Fenton oxidation process was applied to this ACU using Fenton's reagents H_2O_2 and $FeSO_4$, H_2O_2 and CuCl, and H_2O_2 and AC.

Analytical Methods

The concentration of drugs in the artificially contaminated water or urine was detected immediately at the end of each experiment using UV-VIS double beam spectrophotometer. The pH and the COD were determined according to the standard methods. Final COD was quantitatively corrected for hydrogen peroxide interference according to the correlation equation (Kang et al., 1999).

Result and Discussion

Factors affecting the Performance of Fenton's process

Effect of pH

Results indicated that the optimum pH of Fenton's Oxidation ranged from and 3.0 to 3.5. This is in good agreement with (Tekin et al., 2006). When pH > 3, oxidation efficiency rapidly decreases due to auto decomposition of H_2O_2 affecting the production of OH radicals (Tekin et al., 2006) and deactivation of ferrous catalyst with the formation of ferric hydroxide precipitates (Luis et al., 2009). It was confirmed that there is a decrease in oxidation potential of hydroxyl radical by increasing the pH value (Lucas and Peres, 2006). When pH is < 3, the reaction of H_2O_2 with Fe^{2+} was seriously

Figure 1: Urine diverting toilet.

affected to reduce hydroxyl radical production and water was formed by the reaction of OH radicals with H^+ ions (Lucas. and Peres, 2006) and also there was an inhibition for the radical forming activity of iron (Luis et al., 2009).

Effect of H_2O_2 and Ferrous Sulphate

The overall effect of sulphates on degradation rates is much lower in comparison to chloride ions. Moreover, ferrous sulphate is more reactive towards hydrogen peroxide than ferrous ions alone that can additionally balance inhibitory potential of the sulphate ions (Laat et al., 2004)

To investigate the optimum dose of H_2O_2, variable H_2O_2 concentrations ranging from 150 to 800 mg/L were added at constant iron concentrations (150 mg/L). The optimum dose of H_2O_2 was found to be 750 mg/L at which the removal rate of the selected PhACs and COD reached the maximum (Table 1 and Figure 2).
The experiment was extended to investigate the optimum dose of Fe^{2+}. Therefore, variable Fe^{2+} concentration ranging from 10 to 150 mg/L, at optimum concentrations of hydrogen peroxide (750 mg/L) were examined (Table 2). The optimum dose of Fe^{2+} was found to be 130 mg/l at which the optimum removal rate of PhACs and COD was achieved (Table 2).

Effect of H_2O_2 and CuCl

Variable doses of CuCl ranging from 10 to 150 mg/L were examined at the predetermined optimum dose of H_2O_2 (750 mg/L) for the determination of the optimum dose of CuCl. The results showed that the optimum dose of the CuCl is 100 mg/L Cu^{+1} at which the removal rate ranged from 95 to 98% for the PhAC's and 97% for the COD (Table 3).

Effect of H_2O_2 and AC

Variable doses of the H_2O_2 ranging from 500 to 5000 mg/L, at a constant dose of PAC (4000 mg/L) were examined to determine the optimum dose of H_2O_2 (Figure 3). It was found that 4000 mg/L H_2O_2 is the optimum dose (Table 4). To determine the optimum dose of AC different doses of AC varying from 100 to 4000 mg/L, at the predetermined optimum concentrations of H_2O_2 (4000 mg/L) were investigated. Results indicated that the optimum dose of AC is 3000 mg/L at which the removal rate ranged from 97 to 99% for the PhACs and 97% for the COD (Table 5).

Artificially contaminated urine (ACU):

Urine samples were artificially contaminated with 40 mg/l of each of the selected PhACs in combination. By contaminating the raw urine, increase in the COD was recorded. Correlation between the chemical characteristics of the raw urine and the ACU (Table 6) showed an increase from 6660 to 13400 mg/l for the COD (total) and from 4130 to 7150 for COD (dissolved) (Table 6). The rest of characteristics remained the same.

Effect of the predetermined doses on the ACU

These predetermined doses are: (750 mg/L H_2O_2 & 130 mg/L $FeSO_4$) as combination (1), (750 mg/L H_2O_2 & 100 mg/L CuCl) as combination (2) and (4000 mg/L H_2O_2 & 3000 g/L AC) as combination (3). When combination (1) was examined unsatisfied removal rate was obtained namely, 86.2%, 45.8%, 70% and 80% for the COD, LEF, IBP and ATV respectively (Table 7). Similar unsatisfied removal rates were obtained by using either combination (2) or combination (3) (Table 7).

The impact of these predetermined doses on the characteristics of the ACU is given in Table 6. Results exhibited decrease in CODT, CODD, BOD_5, TP, NO_3, NO_2, k and Na due to the effect of oxidation. Slight increase in the Ca concentration was recorded which could be attributed to the release of Ca from the oxidation of atorvastatin (as being a calcium salt).

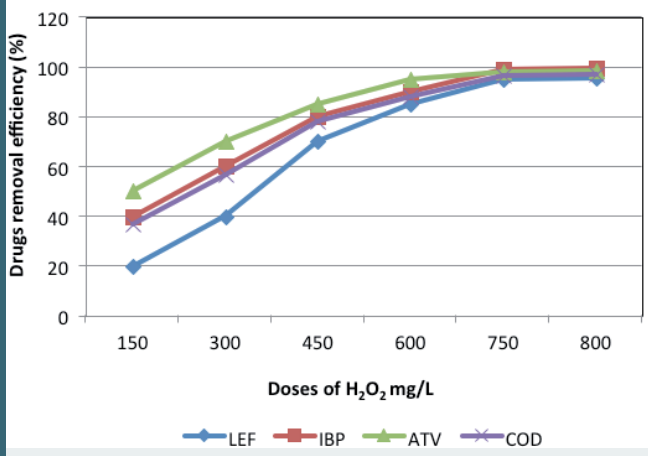

Figure 2: Effect of Fenton process (at different H_2O_2 doses) and constant dose of $FeSO_4$ (150 mg/L) on the removal of the selective PhACs and elimination of COD from water.

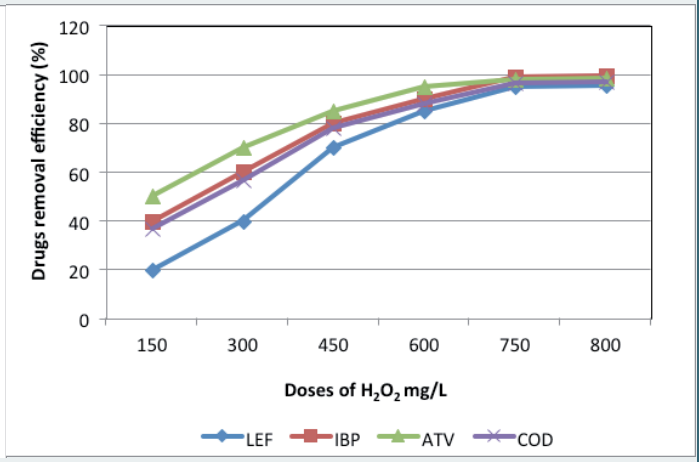

Figure 3: Effect of different doses of hydrogen peroxide in combination with constant dose of powdered activated carbon (AC = 4000 mg/L) on the removal of PhACs and COD from aqueous solution.

Effect of Higher Doses on the Artificially Contaminated Urine

Higher doses namely, (1000 mg/L H_2O_2 &150 mg/L $FeSO_4$) as combination (4), (1000 mg/L H_2O_2 & 150 mg/L CuCl) as combination (5) and (5000 mg/L H_2O_2 & 4000 mg/L AC) as combination (6) were examined to improve the removal rate of the PhACs. Results obtained showed that removal efficiency of PhACs was notably increased (Table 7). When combination (4) was employed the achieved elimination rate increased from 86.2 to 98.6% for COD, from 45.8 to 95% LEF, from 70 to 98% for IBP and from 80 to 99% for ATV. Similar improvements were achieved by employing the other combinations (5) and (6) (Table 7).

Impact of these higher doses on the chemical characteristics of ACU indicated further decrease in CODT, CODD, BOD_5, TP, NO_3, NO_2, k and Na (Table 6). However, higher increase in the Ca concentration as a result of higher release from the atorvastatin (Table 6).

It is worth mentioning that combination (4) and combinations (5) are at the same concentration. However, combination (4) was slightly more efficient in the elimination of the PhACs. Therefore, combination (4) is more preferable than combinations (5) (Figure 4).

The overall results indicate that the Fenton's oxidation process gives high removal efficiency when applied on the artificial contaminated urine, where 95%, 98%, 99% and 98.6% removal efficiency of levofloxacin, ibuprofen, atorvastatin and COD respectively, were achieved under operating condition: pH 3 and combination (4) (Table 7). When combinations (5) was examined at pH 3, less slight removal rate was achieved, namely 93%, 96%, 98% and 97% for levofloxacine, ibuprofen, atorvastatin and COD respectively. By employing AC at combinations (6) and at pH 3, removal efficiency reached 90%, 95%, 96% and 96.8 % for levofloxacine, ibuprofen and atorvastatin and COD, respectively (Figure 4). In the case of AC the

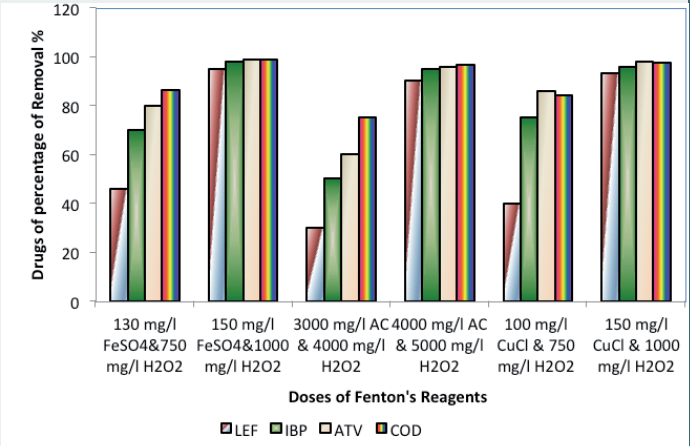

Figure 4: Effect of different Fenton reagents on the elimination of PhACs and COD from artificial contaminated urine sample.

removal is due to both adsorption (Eq 5,6) and catalytic reaction (Eq 7,8) (Georgi and Kopinke, 2005).

Conclusion

Fenton's treatment may be rated as uneconomical for the large volumes of urine. However, Fenton oxidation is preferable as an effective pre-treatment method for the non-biodegradable portions, which renders them more biodegradable for following biological processes. In the case of pre-treatment, lower dose of Fenton's reagents can be used. Therefore, urine can be used safely for agriculture purpose without the hazard of pharmaceuticals. It is worth mentioning that the catalysts (Fe^{2+} or Cu^{1+}) are more efficient than AC for the elimination of PhACs as lower concentrations of H_2O_2 are required.

Table 1. Efficiency of Fenton treatment at variable doses of H_2O_2 and constant dose of $FeSO_4$ (150 mg/L) for aqueous synthetic sample

Doses of H_2O_2 (mg/L)	COD		LEF		IBP		ATV	
	(mg/L)	(%) removal	(mg/L)	(%) removal	(mg/L)	(%) removal	(mg/L)	(%) removal
0	7200	0	40	0	40	0	40	0
150	4536	37	32	20	27.2	40	20	50
300	3132	56.6	24	40	16	60	12	70
450	1584	78	12	70	8	80	6	85
600	864	88	6	85	4	90	2	95
750	252	96.5	2	95	0.4	99	0.8	98
800	216	97	1.8	95.5	0.2	99.5	0.6	98.5

Table 2: Efficiency of Fenton treatment at variable doses of $FeSO_4$ in combination with the optimum dose of H_2O_2 (750 mg/L) for aqueous synthetic sample

Doses of $FeSO_4$ (mg/L)	COD		LEF		IBP		ATV	
	(mg/L)	(%) removal	(mg/L)	(%) removal	(mg/L)	(%) removal	(mg/L)	(%) removal
0	7200	0	40	0	40	0	40	0
10	3384	53	28	30	16	60	12	70
40	2475	65.6	20	50	12	70	8	80
70	1584	78	12	70	8	80	6	85
100	792	89	6	85	2.8	93	4	90
130	231	96.8	2.2	94.5	0.6	98.5	1	97.5
150	216	97	2	95	0.4	99	0.7	98

Table 3: Efficiency of Fenton treatment by addition of different doses of CuCl at optimum dose of H_2O_2 (750 mg/L) for aqueous synthetic sample.

Doses of CuCl (mg/L)	COD		LEF		IBP		ATV	
	(mg/L)	(%) removal	(mg/L)	(%) removal	(mg/L)	(%) removal	(mg/L)	(%) removal
0	7200	0	40	0	40	0	40	0
10	4104	43	32	20	20	50	16	60
40	2520	65	20	50	12	70	10	75
70	1368	81	12	70	6	85	5.2	87
100	216	97	2	95	1.2	97	1.2	98
130	144	98	1.6	96	0.8	98	0.8	97
150	108	98.5	1.2	96.5	0.6	98.5	0.5	97.5

Table 4: Efficiency of Fenton treatment process using variable doses of H_2O_2 at constant dose of AC (4000 mg/L) for aqueous synthetic sample.

Doses of H_2O_2 (mg/L)	COD		LEF		IBP		ATV	
	(mg/L)	(%) removal	(mg/L)	(%) removal	(mg/L)	(%) removal	(mg/L)	(%) removal
0	7200	0	40	0	40	0	40	0
500	5292	26.5	36	10	28	30	24	40
1000	3240	55	24	40	16	60	14	65
2000	1548	78.5	12	70	6	85	8	80
3000	648	91	6	85	2.8	93	2	95
4000	144	98	1.48	96.3	0.8	98	0.6	98.7
5000	108	98.5	1.4	96.5	0.6	98.5	0.4	99

Table 5: Efficiency of Fenton treatment process at different doses of AC in combination with the optimum dose of H_2O_2 (4000 mg/L) for aqueous synthetic sample.

Doses of AC (mg/L)	COD		LEF		IBP		ATV	
	(mg/L)	(%) removal	(mg/L)	(%) removal	(mg/L)	(%) removal	(mg/L)	(%) removal
0	7200	0	40	0	40	0	40	0
100	3672	49	25	37.3	20	50	16	60
500	1764	75.5	11.6	71	10	75	8	80
1000	432	94	2.8	93	2.16	94.6	2	95
2000	288	96.5	2	05	1.6	96	1.2	97
3000	144	98	1.2	97	1	97.5	0.4	99
4000	108	98.5	1	97.5	0.8	98	0.32	99.5

Table 6: Characteristic of urine before and after treatment using (FeSO4 and H2O2), (AC and H_2O_2) and (CuCl and H_2O_2) (as mg/l).

Parameter	Natural human urine	Artificially contaminated urine	Fenton's reagents doses (mg/L)					
			750 H_2O_2 130 $FeSO_4$ Comb. (1)	1000 H_2O_2 150 $FeSO_4$ Comb. (4)	750 H_2O_2 100 CuCl Comb. (2)	1000 H_2O_2 150 CuCl Comb. (5)	4000 H_2O_2 3000 AC Comb. (3)	5000 H_2O_2 4000 AC Comb. (6)
pH	4.95	4.14	9.5	9.5	9.5	9.5	9.5	9.5
COD_T (mg/L)	6555	13355	1840	188	2100	346	3970	415
COD_D (mg/L)	4130	7153	1160	118	1320	218	3300	260
COD_D (mg/L)	1200	1205	370	144	362	180	421	241
BOD_5/COD	0.18	0.09	0.20	0.76	0.17	0.52	0.10	0.58
T.P. (mg/L)	449	450	90	17	113	41.1	130	32.8
NO_3 (mg/L)	4.46	4.47	0.107	0.028	2.990	2.480	2.233	1.781
NO_2 (mg/L)	17.56	18	3.6	0.3	4.3	1.2	5.2	2.3
K (mg/L)	13886	13890	7630	1888	6500	1586	2057	773
Na (mg/L)	14760	14770	8410	1745	*7800*	1615	2610	831
Ca (mg/L)	5825	5820	6015	9240	5900	8610	8255	4940

Table 7: Efficiency of Fenton treatment process on the removal of PhACs from artificial contaminated urine sample using different Fenton's reagents.

Doses of Fenton's reagents			COD		LEF		IBP		ATV	
H_2O_2 (mg/L)	Reagent	Combination	(mg/L)	(%) removal	(mg/L)	(%) removal	(mg/L)	(%) removal	(mg/L)	(%) removal
0	0	-	13355	0	40	0	40	0	40	0
750	130 mg/L $FeSO_4$	1	1840	86	21.7	46	12	70	8	80
1000	150 mg/L $FeSO_4$	4	188	99	2	95	0.8	98	0.4	99
750	100 mg/L CuCl	2	2100	84	24	40	10	75	5.6	86
1000	150 mg/L CuCl	5	346	97	2.8	93	1.6	96	0.8	98
4000	3000 mg/L AC	3	3300	75	28	30	20	50	16	60
5000	4000 mg/L AC	6	415	97	4	90	2	95	0.6	96

References

Abdel-Shafy, H.I., Guindi, K.A., Tawfik, N.S. (2008): Groundwater Contamination as Affected by Long-Term Sewage Irrigation in Egypt. In: Al Baz, I., Otterpohl, R., Wendland, C. (Eds): Efficient Management of Wastewater and Reuse in Water Scarce Countries, Springer Publishers, Netherlands, pp.53-65.

Abdel-Shafy, H.I., El-Khateeb M.A., Nashy E.Sh. (2010): Advanced Oxidation Reaction for the Treatment of Leather Liming / Unhairing Wastewater. In: Proceeding of 4th International Conference, Environmental Science and Technology, 14-16 December 2010, Cairo, Egypt.

Dolliver, H., Kumar, K., Gupta, S. (2007): Sulfamethazine Uptake by Plants from Manure Amended Soil. J. Environ. Qual. 36 (4), 1224-1230.

Geisslinger, G., Dietzel, K., Bezler, H., Nuernberg, B., Brune, K. (1989): Therapeutically Relevant Differences in the Pharmacokinetical and Pharmaceutical Behavior of Ibuprofen Lysinate as Compared to Ibuprofen Acid. International Journal of Clinical Pharmacology, Therapy, and Toxicology 27(7), 324-328.

Georgi, A., Kopinke, F.D. (2005): Interaction of adsorption and catalytic reactions in water decontamination processes. Part I. Oxidation of organic contaminants with hydrogen peroxide catalyzed by activated carbon. Applied Catalysis B: Environmental 58, 9-18.

Ikehata, K., Naghashkar, N.J., Ei-Din, M.G. (2006): Degradation of Aqueous Pharmaceuticals by Ozonation and Advanced Oxidation Processes: A Review. Ozone Sci. Eng. 28, 353-414.

Kang Y. W., Cho M. J., Hwang, K. Y. (1999): Correction of Hydrogen Peroxide Interference on Standard Chemical Oxygen Demand Test. Water Res. 33(5), 1247-1251.

Klavarioti, M., Mantzavinos, D., Kassinos, D. (2009): Removal of Residual Pharmaceuticals from Aqueous Systems by Advanced Oxidation Processes. Environ. Int. 35, 402-417.

Laat J. D., Troung G. L. and Legue B. (2004): A comparative study of the effects of chloride, sulfate and nitrate ions on the rates of decomposition of H2O2 and organic compounds by Fe(II)/H2O2 and Fe (III)/H2O2. Chemosphere 55, 715

Lienert, J., Güdel, K., Escher, B. (2007): Screening Method for Ecotoxicological Hazard Assessment of 42 Pharmaceuticals Considering Human Metabolism and Excretory Routes. Environ. Sci. Technol. 41 (12), 4471-4478.

Lucas, M.S., Peres, J.A. (2006): Decolorization of The Azo Dye Reactive Black 5 by Fenton and Photo-Fenton Oxidation. Dyes and Pigm. 71, 236-244.

Luis, A.D., Lombranda, J.I., Varona, F., Menendez, A. (2009): Kinetic Study and hydrogen peroxide consumption of phenolic compounds oxidation by Fenton's reagent. Korean. J. Chem. Eng. 26(1), 48-56.

McCrindle, B.W., Ose, L., Marais, A.D. (2003): Efficacy and Safety of Atorvastatin in Children and Adolescents with Familial Hypercholesterolemia or Severe Hyperlipidemia: A Multicenter, Randomized, Placebo-Controlled Trial. J. Pediatr. 143(1), 74-80.

Mira P., Jelena R. and Damia B. (2011): Advanced Oxidation Processes (AOP) Applied for

Wastewater and Drinking Water Treatment: Elimination of Pharmaceuticals. The Holistic Approach to Environment 1(2), 63-74.

Musson, S.E., Townsend, T. G. (2009): Pharmaceutical Compound Content of Municipal Solid Waste. J. Hazard. Mater. 162, 730-735.

Nelson, J. M., Chiller, T. M., Powers, J. H., Angulo, F.J. (2007): Fluoroquinolone-Resistant Campylobacter Species and The Withdrawal of Fluoroquinolones from Use in Poultry: A Public Health Success Story. Clin. Infect Dis. 44(7), 977–80.

Sanderson, H., Brain, R., Johnson, D., Wilson, C., Solomon, K. (2004): Toxicity Classification and Evaluation of four Pharmaceuticals Classes: Antibiotics, Antineoplastics, Cardiovascular, And Sex Hormones. Toxicology 203(1-3), 27-40.

Su, P. H., Chen, J. Y., Su, C. M., Huang, T. C., Lee, H. S. (2003): Comparison of Ibuprofen and Indomethacin Therapy for Patent Ductus Arteriosus in Preterm Infants. Pediatrics International 45(6), 665-670.

Talinli, I., Anderson, G.K. (1992): Interference Of Hydrogen Peroxide on The Standard COD Test. Water Res. 26, 107-110.

Tekin, H., Bilkay, O., Ataberk, S.S., Balta, T.H., Ceribasi, I.H., Sanin, F.D., Dilek, F.B., Yetis, U. (2006): Use Of Fenton Oxidation to Improve the Biodegradability of a Pharmaceutical Wastewater. J. Hazard. Mater. 136, 258-265.

Ternes, T.A., Joss, A., Siegrist, H. (2004): Scrutinizing Pharmaceuticals and Personal Care Products in Wastewater Treatment. Environ. Sci. Technol. 392- 399

Van Esch, A., Van Steensel-Moll, H.A., Steyerberg, E.W., Offringa, M., Habbema, J. D., Derksen-Lubsen, G. (1995): Antipyretic Efficacy of Ibuprofen and Acetaminophen in Children with Febrile Seizures. Archives of Pediatrics & Adolescent Medicine 149 (6), 632–7.

Vieno, N.M., Harkki, H., Tuhkenan, T., Kronberg, L. (2007): Occurrence of Pharmaceuticals in River Water and Their Elimination in a Pilot-Scale Drinking Water Treatment Plant. Environ. Sci. Technol. 41(14), 5077-5084.

Vinnerås, B., Jönsson, H. (2002): The Performance and Potential of Faecal Separation and Urine Diversion to Recycle Plant Nutrients in Household Wastewater. Bioresour. Technol. 84 (3), 275-282.

Wilsenach, J.A., van Loosdrecht, M.C.M.(2006): Integration of Processes to Treat Wastewater and Source-Separated Urine. J Environ Eng 132 (3), 331-341.

Winker, M., Tettenborn, F., Faika, D., Gulyas, H., Otterpohl, R. (2008): Comparison of Analytical and Theoretical Pharmaceutical Concentrations in Human Urine in Germany. Water Res. 42(14), 3633-3640.

Yanga, L., Yua, L. E., Rayb, M. B. (2008): Degradation of Paracetamol in Aqueous Solutions by TiO2 Photocatalysis. Water Res. 42, 3480 – 3488.

Zwiener, C., Frimmel, F.H. (2000): Oxidative Treatment of Pharmaceuticals in Water. Water Res. 34, 1881-1885.

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