CHEMICAL ENGINEERING TRANSACTIONS
VOL. 32, 2013
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-23-5; **ISSN** 1974-9791
DOI: 10.3303/CET1332085

Removal of Xenobiotic Compounds from Wastewater for Environment Protection: Treatment Processes and Costs

Paolo Roccaro*, Massimiliano Sgroi, Federico G. A. Vagliasindi

Department of Civil and Environmental Engineering, University of Catania, Viale A. Doria 6, 95125, Catania, Italy
proccaro@dica.unict.it

Although the technologies available today can produce high quality water even from wastewater, most wastewater treatment plants are not designed to remove emerging xenobiotic contaminants such as endocrine disrupting compounds (EDCs) and pharmaceutical and personal care products (PPCPs). The majority of EDCs and PPCPs are more polar than most regulated contaminants and several have acidic or basic functional groups. EDCs and PPCPs properties, together with their occurrence at trace levels, create unique challenges for the removal processes and the consequent upgrading of wastewater treatment plants. Therefore, in this study ten different wastewater treatment trains are proposed in order to upgrade the conventional wastewater treatment plants. These schemes are based on the multi-barrier concept and include different advanced treatment processes such as membrane processes (membrane bio-reactors, nanofiltration, and reverse osmosis), adsorption on activated carbon (GAC) or biological activated carbon (BAC), advanced oxidation processes (AOPs). Based on the existing data on the effectiveness of these treatment processes for the removal of EDCs and PPCPs, the proposed treatment schemes appear very effective in the removal of a wide range of compounds at trace levels in domestic wastewater. In order to evaluate and compare the feasibility of the proposed different treatment schemes the cost per cubic metre of treated water (Total Unit Cost, TUC) was calculated for several sizes of plant. Therefore, obtained cost functions may be used to estimate the treatment cost for the upgrade of the plant size of interest.

1. Introduction

The occurrence of xenobiotic contaminants at trace level in treated wastewater is of concern for human health and the aquatic ecosystem. PPCPs and EDCs have become highly important emerging contaminants in the last decades because of their detection in virtually all environmental waters at sub-micrograms per litre concentrations, thanks to the more sensitive analytical instruments. Several PPCPs and EDCs have toxic effects to wildlife and to human and the release of antibiotics in the environment may cause the development of bacterial resistance. As a consequence, scientists and regulators are concerned about what level of risk may be associated with the presence of PPCPs and EDCs in drinking water, not to mention their profound effects on wildlife. Many PPCPs and EDCs are ubiquitous in wastewater at ppb and ppt concentration due to their incomplete removal in wastewater treatment plants or point-source inputs. These pollutants may contaminate the receiving freshwater treatment plants and may generate a risk for human health (Benotti et al., 2009). Therefore, as more information is gathered regarding their environmental and health impacts, wastewater treatment plants may need to be upgraded in order to remove these contaminants. The objectives of this study are: i) to evaluate appropriate treatment schemes, based on a literature review, in order to remove PPCPs and EDCs and ii) to assess and compare the costs of the treatment trains.

2. Removal of EDCs and PPCPs: a literature review

Several studies have already tackled or are examining the behaviour of PPCPs and EDCs in conventional treatment trains and in advanced processes. EDCs and PPCPs include a wide range of compounds with different chemical and physical proprieties that affect their removal. Following is described a short literature review on the removal of PPCPs and EDCs from water by using different treatment processes.

2.1 Biological processes

In biological processes, the removal efficiency of EDCs and PPCPs is related to hydrophobicity and to consequent adsorption in activated sludge, whereas more polar compounds are released in the effluent (Heidler and Halden, 2008). Higher removal could be achieved with elevated sludge retention time (SRT) and hydraulic retention time (i.e. achieving nitrification). Membrane bio-reactor (MBR) systems result in higher biodegradation of the more hydrophobic and biodegradable EDCs and PPCPs. Indeed, higher SRT, better conditions of microorganism growth and biological diversity can lead to higher organic micropollutants removal (Petrovic et al., 2003).

2.2 Conventional physical-chemical processes

Surface water conventional treatments (i.e. coagulation, sand filtration, softening), frequently used as tertiary wastewater treatments, are inefficient for the removal of organic micropollutants. Particularly, the use of aluminium sulphate, ferric chloride or lime removes less than 20 % of many EDCs and PPCPs (Westerhoff et al., 2005).

2.3 Adsorption and biological activated carbon

Advanced treatments with high removal efficiencies of emerging contaminants are adsorption on activated carbon, nanofiltration (NF) and reverse osmosis (RO) (Snyder et al., 2007). The performance of activated carbon depends on the properties of the activated carbon sorbent (surface area, pore size distribution, surface charge, oxygen content) and on the properties of the solute (shape, size, charge and hydrophobicity). Hydrophobic interactions are the dominant mechanisms of removal for most organic compounds in activated carbon adsorption systems. However, ion exchange interactions can result in removal of polar solutes. As a result of the hydrophobic interactions, activated carbon efficiently removes most nonpolar organic compounds. The ability of activated carbon to remove most polar compounds will depend upon the strength of the polar interactions. Natural organic matter (NOM) in water competes for adsorption sites and decreases the activated carbon capacity for micropollutants. Adsorption on granular activated carbon (GAC) is effective although with some limitation such as the rapid breakthrough of the more hydrophilic compounds and the regeneration/replacement will be critical for excellent removal (Snyder et al., 2003). Biological activated carbon (BAC) consists of a pre-ozonation followed by a GAC filter which supports the growth of bacteria. This technology has been used for drinking water treatment and has proven to be able to significantly remove natural organic matter, ozonation by-products, disinfection by-products precursors as well as odour and taste compounds. Recently, it has been reported that BAC systems are very effective to remove EDCs and PPCPs (Gerrity et al., 2011; Reungoat et al., 2011). However, more studies are needed for a better evaluation of BAC removal efficiencies taking into account several operating conditions through full-scale applications.

2.4 Membrane processes

Membranes are an effective mean to reduce the concentrations of several EDCs and PPCPs from drinking water and wastewater. The removal rate is related to membrane characteristics and to molecular properties of particular contaminant. Microfiltration and ultrafiltration were found to show a poor removal of most organic micropollutants; however, some loss of steroidal type compounds was observed. By contrast, nanofiltration and reverse osmosis are very effective, with nanofiltration processes having a similar performance compared to the more expensive RO process (Snyder et al., 2007). Particularly, the molecular weight cut off (MWCO) is the parameter that most influenced the removal efficiencies of nanofiltration membrane processes. However, the NF/RO processes produce a large amount of concentrate whose treatment and disposal is very expensive, therefore their application is less suitable in inland areas.

2.5 Disinfection/oxidation and AOPs

The typical doses used in disinfection by UV irradiation (< 40 mJ/cm^2) are unable to remove EDCs and PPCPs (removal efficiencies are often less of 20%) (Rosario-Ortiz et al., 2010). Ozone and chlorine oxidation are selective for the chemical structure and functional groups of PPCPs and EDCs, whose removal range between <10% to >90% with a prominent efficiency of ozonation (Westerhoff et al., 2005). However, chlorination and ozonation are known to lead to the formation of by-products that account for largely unidentified compounds to date. This issue raises concerns regarding their potential impact on the environment and human health. The AOPs, including ozonation which produces OH radicals in wastewater application, are able to degrade a wide range of emerging contaminants thanks to the not selective oxidation produced by the OH radical. Overall, AOPs can achieve high removal of emerging contaminants without producing residuals (e.g. sludge, concentrate). The efficacy of oxidation processes for the removal of pharmaceuticals from wastewater is a function of not only the concentration of EfOM but also its inherent reactivity towards $^{\cdot}OH$. The EfOM properties have been shown to influence the scavenging rate of the OH radical. The scavenging rate is also due to the alkalinity and nitrite levels (Rosario-Ortiz et al., 2010). Table 1 summarizes the range of efficiencies, based on the aforementioned literature review, for the removal of EDCs and PPCPs from different water qualities (river water, ground water, wastewater, synthetic water), at different scale (bench scale, pilot scale, full scale) by using dissimilar water treatment processes.

Table 1: Removal efficiencies (%) of EDCs and PPCPs in wastewater and drinking water by different water treatment processes

Compound	AS/ MBR	AC	BAC	NF/ RO	C/F/S	Cl_2/ ClO_2	O_3	AOPs
Pharmaceuticals								
Acetaminophen	>90	40-70	>70	20-90	<20	>90	>90	>90
Amoxicillin	>70	40-70	>90	>40	<40	>90	>90	20-90
Carbamazapine	<20	>40	>70	>40	<20	0-100	>90	20-90
Diclofenac	<20	<20	>70	>40	<20	>70	>90	>90
Erythromycin	0-100	40-70	>90	>40	<40	>90	>90	20-90
Fluoxetine	>70	>70	>70	>70	<20	<70	>90	>90
Gemfibrozil	>40	20-90	>90	>40	<20	>40	>90	>90
Ibuprofen	>40	<40	>70	>90	<20	20-90	70–90	70–90
Meprobamate	<20	20-40	>70	>40	<20	<20	20-70	20-90
Naproxen	40-70	20-70	>70	>70	<20	>70	>90	>90
Sulfamethoxazole	0-100	20-40	>90	>70	<20	>40	>90	>90
Trimethoprim	0-100	40-70	>90	70–90	<20	>40	>90	0-100
Steroids								
17α-estradiol	>90	>90	>90	>70	<40	>90	>90	>90
Estradiol	0-100	0-100	>70	>40	<20	>70	>90	>70
Estriol	>90	20-70	>90	>40	<20	>90	>90	>90
Estrone	0-100	40-70	>90	>40	<20	>70	>90	>90
Ethynylestradiol	>70	20-90	>90	>40	<20	>70	>90	>90
Progesterone	20-90	70–90	>90	>40	<20	<70	>70	>90
Testosterone	>90	70–90	>90	>40	<20	<70	>70	>90
Personal care products								
Galaxolide	40-70	40-70	>70	>70	<20	<70	70–90	20-90
Musk Ketone	>90	40-70	40-70	>70	<20	<20	20-40	40-70
DEET	>90	20-70	>90	>4	<20	<20	40-70	>90
Oxybenzone	>70	>90	>70	>90	<20	>90	>90	20-90
Triclocarban	>70	>70	>70	>70	<40	<70	20-90	20-90
Triclosan	>40	>90	>90	>90	<20	>70	>90	>90
Others (iodinated contrast media, fire retardants, surfactant, plasticizer, etc.)								
Bisphenol-A	>40	20-70	20-70	20-90	<20	40-70	20-90	20-90
Caffeine	>40	20-70	>90	20-90	<20	40-70	70–90	70–90
Iopromide	>90	<40	>70	>40	<20	<70	40-70	20-90
Octylphenol	>40	20-70	20-70	20	<20	40-70	20-90	20-90
Nonylphenol	>40	20-70	20-70	20	<20	40-70	20-90	20-90
TCEP	20-90	20-70	>90	>40	<40	<20	<20	<20

AS: activated sludge, MBR: membrane bio-reactor, AC: activated carbon, BAC: biological activated carbon, NF: nanofiltration, RO: reverse osmosis, C/F/S: coagulation/flocculation/softening, Cl_2/ClO_2: chlorination, O_3: ozonation, AOPs: advanced oxidation processes.

3. Suitable treatment schemes: multi-barrier concept

The existing wastewater treatment plants are usually designed to remove organic substrate, nutrients and pathogens. Due to the continuous discovery of further environmental contaminants which are toxic for both the environment and health, wastewater treatment plants need to be upgraded in order to remove these contaminants, especially when water must be reused. Removal efficiencies of emerging contaminants range according to contaminant characteristics and treatment processes. Generally, conventional treatments of wastewater allow a limited removal of xenobiotic compounds. Therefore, advanced treatments conveniently arranged in treatment trains may be implemented to achieve high removal efficiencies of emerging trace level compounds. Particularly, it needs to prefigure treatment schemes based on multi-barrier concept that involves dissimilar processes whose combination is effective in the removal of a wide range of compounds at trace levels in water. In order to upgrade existent treatment plants, the addition of one or more treatment units according to the multi-barrier concept is a useful strategy to control emerging contaminants. Based on the actual treatment trains used for wastewater treatment worldwide and on the literature review dealing with the removal of PPCPs and EDCs, presented in the previous section, ten treatment schemes were considered in this study and a qualitative assessment about the removal efficiencies of PPCPs and EDCs was provided (Table 2).

Table 2: Selected treatment trains for the removal of PPCPs and EDCs and related efficiencies

Scheme	Treatment processes	Removal efficiency % range	
		UV	AOPs
1	Pre. + Settling + AS + Settling + UV/AOPs	18-94	48-99
2	Pre. + Settling + AS + Settling + Sand filtration + UV/AOPs	18-94	48-99
3	Pre. + Settling + AS + Settling + Sand filtration + GAC + UV/AOPs	24-99	60-99
4	Pre. + Settling + AS + Settling + CP + Sand filtration + GAC + UV/AOPs	29-99	62-99
5	Pre. + Settling + MBR + GAC + UV/AOPs	24-99	60-99
6	Pre. + Settling + MBR + O_3 + BAC + UV/AOPs	84-99	87-99
7	Pre. + Settling + MBR + NF/RO + UV/AOPs	69-99	75-99
8	Pre. + Settling + MBR + O_3 + NF/RO + UV/AOPs	75-99	75-99
9	Pre. + Settling + MBR + GAC + NF/RO + UV/AOPs	69-99	80-99
10	Pre. + Settling + MBR + O_3 + BAC + NF/RO + UV/AOPs	90-99	92-99

Pre: preliminary treatment (screen, grit and oil removal), AS: activated sludge, MBR: membrane bio-reactor, GAC: granular activated carbon, BAC: biological activated carbon, CP: chemical precipitation, NF: nanofiltration, RO: reverse osmosis, AOPs: advanced oxidation processes (O_3, UV/H_2O_2, O_3/H_2O_2).

The UV process, considered in Table 2, is related to typical UV doses required for disinfection (i.e., <40 mJ/cm^2), ineffective to remove most EDCs and PPCPs (Snyder et al., 2003; Rosario-Ortiz et al., 2010). On the other hand, the use of AOPs largely improves the PPCPs and EDCs removal. Conventional biological treatments (Scheme 1 and Scheme 2) show removal efficiencies very variable which rich the high removal efficiency if AOPs are employed. The control of EDCs and PPCPs may be primarily achieved by activated carbon and membrane processes, although the AOPs processes may play an important role to control this contaminant and guarantee the simultaneous water disinfection. Treatment schemes with activated carbon process (Scheme 3 and Scheme 5) could be a suitable solution to control EDCs and PPCPs in small plants, due to their lower capital and operation and maintenance costs. The use of MBR systems improves the biological removal of some xenobiotic compounds. The use of chemical precipitation processes is an ineffective option but is included in the Scheme 4 because several wastewater treatment plants that produce reclaimed water employ this process to remove metals, hardness, etc. The schemes with BAC or membrane processes (Scheme 6, Scheme 7 and Scheme 8) may be a very effective option to remove xenobiotic contaminants. The use of pre-ozonation in scheme 8 is useful to remove emerging contaminants while controlling the membrane fouling. The schemes with both activated carbon (or biological activated carbon) and NF/RO processes (Scheme 9 and 10) are the most effective to remove xenobiotic compounds at trace levels, but very expensive. Overall, the wide range of removal efficiency reported in Table 2 is due to the fact that some compounds are “easy to remove” while others are more recalcitrant to some treatment processes as shown in Table 1. For instance, Scheme 1 and 2 can remove the emerging contaminants basically thanks to the biodegradation, therefore very high removal efficiency will be obtained for selected compounds which are susceptible to biological removal. Treatment trains employing UV disinfection as final treatment unit will not have a benefit in terms of emerging contaminants removal, while the use of AOPs improves the efficiency. In particular, it is to be highlighted that AOPs carried out with a ozone to TOC ratio ranging between 0.5 and 1.0 mg per mg can result in very high degradation (up to >90% for $O_3/TOC=1$) for most emerging contaminants, while the UV/H_2O_2 efficiency is usually lower and is more affected by the influent water quality (e.g. UV transmittance). Furthermore, the specific cost for the energy consumption for UV/H_2O_2 is higher than those for either O_3/H_2O_2 or for ozone oxidation. However, UV/H_2O_2 would be a viable solution for degradation of organic micropollutants in waters with high bromide content, because UV/H_2O_2 excludes bromate formation.

4. Treatment costs

Estimated costs of wastewater treatment trains represent an important aspect to assess the feasibility and sustainability of wastewater treatment projects for the protection of environment and health. In order to evaluate and compare the feasibility of the selected treatment schemes, capital costs, operation and maintenance costs (O&M) and total unit costs (TUC) have been calculated for each treatment train, considering five different sizes (8,000, 15,000, 60,000, 110,000, 200,000 equivalent population related to a water supply of 180, 200, 250, 275, 300 L per capita per day, respectively). The total unit cost (TUC) is a useful parameter for a direct comparison of the treatment costs of different schemes. The treatment costs were computed based on actual price whenever possible according to the methodology proposed by Roccaro and Vagliasindi (2007). The capital costs include construction costs of building works, costs of electromechanical components, taxes, design costs, contingency costs, etc. The operation and maintenance costs include costs for personnel, energy, reagents, sludge disposal and ordinary and extraordinary repairs. These costs were assessed according to metric estimates, data provided by companies, data based on the literature review and simplify estimates (Roccaro and Vagliasindi, 2007). In the costs calculation, biological processes included nitrogen and phosphorus removal. For the UV disinfection a dose of 20 mJ/cm^2 was considered, while the advanced oxidation processes examined were ozonation (5 mg/L), UV/H_2O_2 (500-700 mJ/cm^2 and 5 mg/L of H_2O_2) and O_3/H_2O_2 (3-5 mg/L of O_3 and 5 mg/l of H_2O_2), according with typical water treatment doses (Rosario-Ortiz et al., 2010; Gerrity et al., 2011; Katsoyiannis et al., 2011). The energy requirements for ozonation and advanced oxidation processes mainly depend on the OH radical scavenging rate of the water and type of micropollutant to be treated (Katsoyiannis et al., 2011). In this study energy consumptions considered were 0.3 kWh/m^3 for O_3, 0.35 kWh/m^3 for O_3/H_2O_2 and 0.9 kWh/m^3 for UV/H_2O_2. The total unit cost was computed by the operation and maintenance costs and annual depreciation charge of capital costs as shown in Eq (1).

$$TUC = \frac{ADC + OMC}{Q} \tag{1}$$

ADC = annual depreciation charge of capital costs (€/y);
OMC = operation and maintenance costs (€/y);
Q = flow rate (m^3/ y).

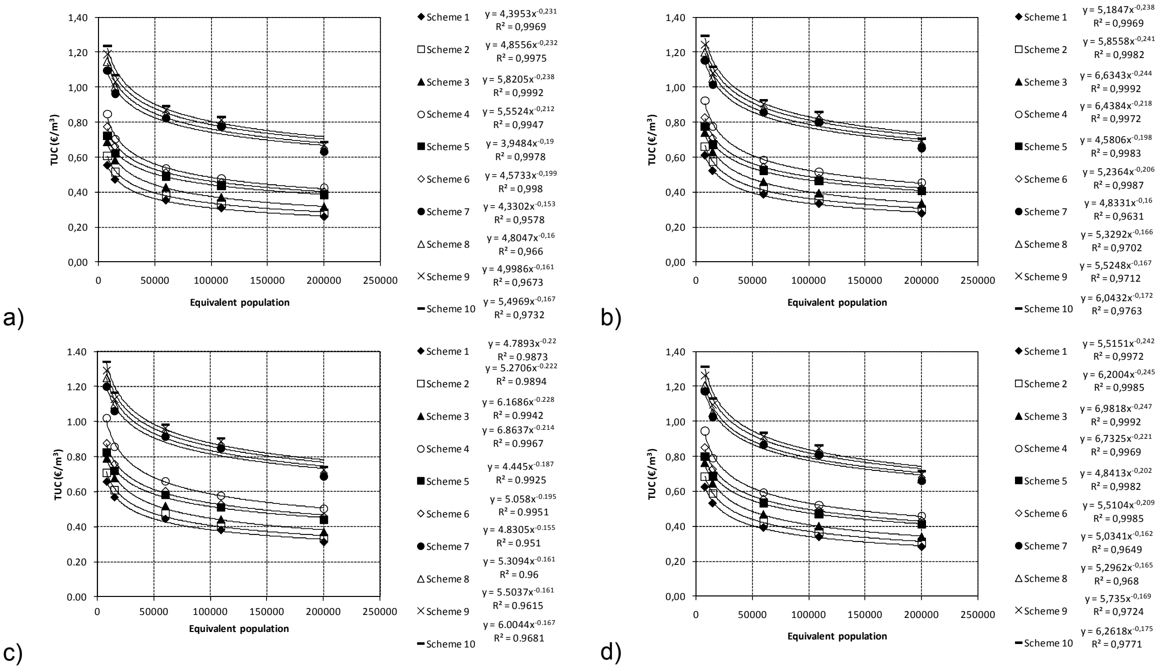

Figure 1: Cost function (total unit cost, €/m^3) for the proposed treatment schemes with a) UV disinfection, b) ozone oxidation, c) UV/H_2O_2 process, d) O_3/H_2O_2 process

In order to calculate the ADC an interest rate of 5.5 % was adopted and a depreciation time of 10 years for electromechanical components and 30 years for civil works were considered.
Figure 1 shows the obtained data of the total unit costs calculated for the five plant sizes considered for each of the ten treatment schemes selected (Table 2) varying the final disinfection/oxidation process (UV, UV/H_2O_2, O_3, O_3/H_2O_2). All data were strongly fitted by power curves resulting in cost functions useful to estimate the treatment cost for the selected treatment scheme and for the plant size of interest. The decrease of the cost functions is a typical power trend due to a scale factor (Roccaro and Vagliasindi, 2007). Overall higher values of the TUC are observed for schemes that include the membrane processes (NF/RO).

5. Conclusions

The removal of xenobiotic trace-level contaminants could be required by the future regulations for the environment and health protection especially in the case of wastewater reclamation and reuse. Technical and economic aspects are important parameters to select an appropriate treatment scheme in order to remove these emerging contaminants. The removal efficiencies of EDCs and PPCPs range a lot with the class of compound and the kind of treatment processes. Schemes based on the multi-barrier concept that involves dissimilar processes are effective in the removal of a wide range of xenobiotic compounds, but have higher capital, operation and maintenance costs than conventional treatment plants. Based on the literature review concerning the removal of target emerging contaminants carried out in this study, it is demonstrated that the control of EDCs and PPCPs may be achieved using different wastewater treatment trains, including a combination of MBR processes, activated carbon, biological activated carbon, membrane processes (NF/RO), oxidation/disinfection processes such as UV and AOPs. Cost curves are presented for the treatment schemes proposed that may help to select the more feasible or sustainable treatment train.

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