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Photochemical advanced oxidation technologies: Emerging contaminants removal

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Résumé

Un processus d'industrialisation continu, une forte urbanisation due à la croissance de la population, la déforestation et la pollution exercent une pression importante sur les ressources d'eau douce. La viabilité à long terme de l'approvisionnement en eau propre est dictée par la protection et la gestion des ressources aquatiques, de l'efficacité de la récupération de l'eau provenant de diverses sources d'effluents. La présence de nombreux composés organiques à l'état de traces, les contaminants émergents,ont été rapportés dans divers rejets d'eaux usées. Les méthodes traditionnelles de traitement tel que la biodégradation secondaire sont incapables d'éliminer bon nombre de ces nouveaux contaminants préoccupants. Les processus d'oxydation avancée , qui produisent des espèces réactives in situ tel que les radicaux hydroxyles ,sont identifiés comme l'une des technologies possibles pour l'élimination des de contaminants organiques récalcitrants présent à des concentrations traces.

Mots-clés:traitement de l'eau, procédé d'oxydation avancée, contaminants émergents, réutilisation des eaux

Abstract

Continuing processes of industrialization and urbanization due to population growth,deforestation, and pollution are exerting pressure on the depleting freshwater resources inmany parts of the world.The long-term sustainability of clean water supply is dictatedby source water protection, management of water resources, and the efficiency of waterreclamation from various effluents.Trace concentrations of numerous organic compounds, emerging contaminants arereported in various wastewater effluents and aquatic systems. The traditional treatment methods such as secondarybiodegradation cannot appreciably remove many of these contaminants of emergingconcern. Advanced oxidation processes, which produce reactive species like hydroxylradicals in-situ, are identified as one of the potential technologies for the removal of traceconcentrations of organics from various water streams.

Keywords:water treatment, advanced oxidation processes, emerging contaminants, water reuse

Introduction

Population growth, increased industrial activities in manyparts of the world as well as the estimated impacts ofclimate change will exceed various pressures on the watersupply systems (EEA 2007).Considering the growingburden on freshwater resources, particularly the over abstractionof groundwater, the deterioration of groundwaterquality, and saltwater intrusion into coastal aquifers,the utilization of alternative water sources is a promising option to supplement water supply and restore naturalresources (EEA 1999).

Global water demand will continue to increase and isexpected to reach probably 70% of the available freshwaterresources till 2025 (UN 2006).The water stress index – the ratio of a country's totalwater withdrawal to its total renewable freshwaterresources – serves as a rough indicator for the pressureexerted on water resources. Not all water uses are causingcomparable stress. A ratio in the range of 10% to 20%indicates that water availability is becoming a constrainton development. A water stress index above 20% issupposed to necessitate comprehensive water managementefforts and actions to resolve conflicts amongcompeting uses (OECD 2003).

In order to alleviate water stress, wastewater effluent is regarded as an alternative. However conventiona activated sludge treatment is efficient for biodegradable substances but meets its limit regarding recalcitrant contaminants.

The U.S Geological survey defines emerging contaminants (ECs) as "any synthetic or naturally occurring chemical or any micro-organism that is not commonly monitored in the environment but has a potential to enter the environment and cause known or suspected adverse ecological or human health effects" (USGS, 2011). In addition, Wong (2006) has defined ECs as "chemicals (including veterinary and human pharmaceuticals) that currently are being used and released into the environment and are of special concern due to widespread occurrence and potential for toxic effects".

1. Water scarcity and wastewater reclamation

Through the water cycle (see Figure 1.a) which consists of precipitation vapor, transport, evaporation, evapo-transpiration, infiltration, groundwater flow and runoff, water is transported from the oceans back to land and precipitates as rain which in turn fills up lakes, rivers and groundwater basins, making it available as freshwater for plants, animals and humans (UNEP, 2010). Nearly 577, 000 km3 of water circulates through the cycle each year. The availability of this freshwater is the driving force in the development of human culture and the access to water has been declared a fundamental human right, but clean water supplies and sanitation is still a major problem.

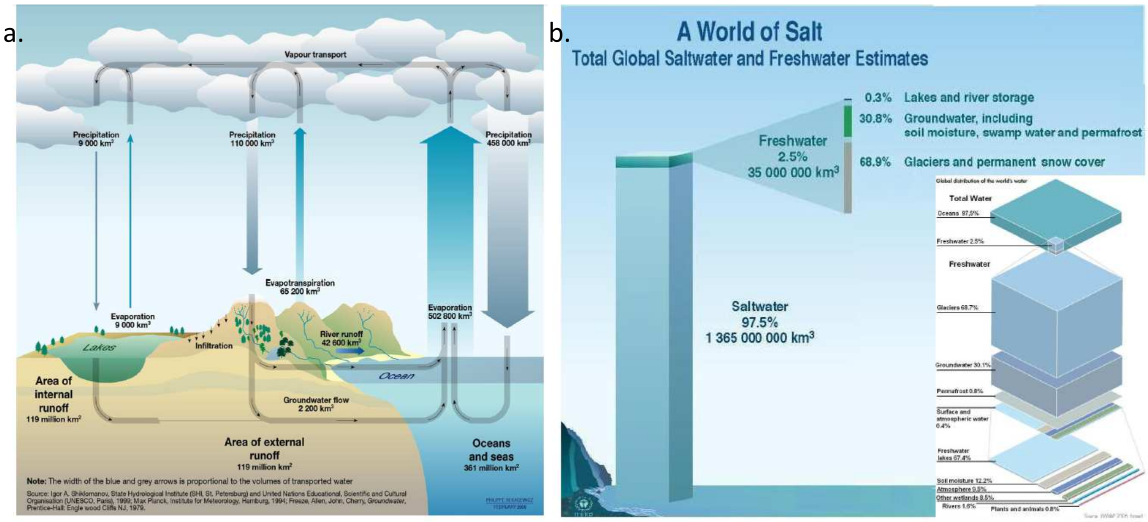

Figure 1 Water on earth (a) The global water cycle and (b) Total global saltwater and freshwater estimates

The water available for drinking supplies (Figure 1b) represents only 2.5% of the volume of the earth. So the seemingly infinite abundant resource is not so abundant at all, and in some places it is becoming increasingly scarce. Actually the relationship between the use and consumption and the extraction of water shows a great gap. The use of fresh water in each continent depends on various socioeconomic factors like development, geographical characteristics, climate and demographic factors. The world’s annual water exploitation has risen between 1995 and 2000 from 3790 km^3 to 4430 km^3 and is expected to raise 10-12% every 1à years to approximately 5240 km3 in 2025.

The raising demand of water, its association with the decline in water quality and contamination are problems which need to be addressed and solved urgently. There are numerous regions in the world where abundant water bodies are contaminated thus are unsuitable for human use.

2. The issue of emerging contaminants in water reuse

According to a review conducted by Asano andCotruvo(2004) the main concerns in indirect potable reuse are healthrisks resulting from pathogens and trace chemicals as well asnitrate. Among the organic pollutants there is a range of socalled emerging contaminants such as endocrine disruptingcompounds, pharmaceutically active compounds, personal care products and disinfectionby-products. The occurrence of these emergingcontaminants (ECs) in the aquatic environment including surfaceand groundwaters, and wastewater sludge as well asdrinking water has been studied (Heberer 2002; Ternes& Joss 2006).
ECs are released into the environment via different sources; Figure 2 shows the possible ways of releasing these contaminants.

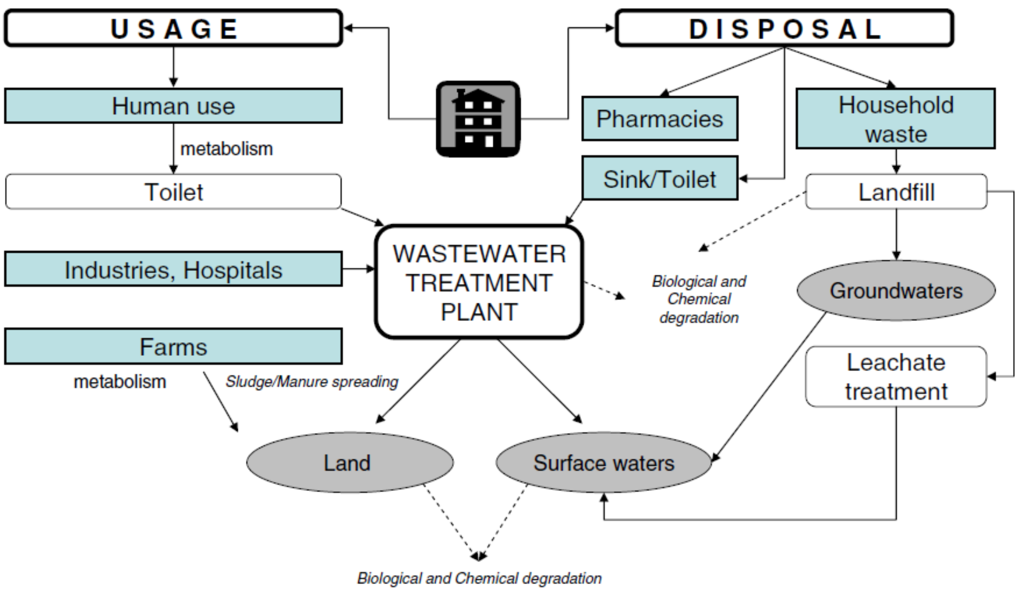

Figure 2. Sources and fate of emerging contaminants in the environment showing the range of possible inputs and receptors

The natural compounds which are hormones are excreted by vertebrates and by some other invertebrates groups (Oehlmann& Schulte-Oehlmann, 2003), while synthetic compounds or man-made compounds can be produced by manufacture. The most relevant microcontaminants which are found in the environment in low concentrations are listed in Table 1 with their most relevant examples.

Emerging Contaminants and other contaminants	
Types	**Example**
Pharmaceuticals	
Veterinary and human antibiotics	Trimetoprim, Erythromycin, Lincomycin, Sulfamethoxazol
Analgesics and anti-inflammatory drugs	Codeine, Ibuprofen, Acetaminophen, Acetylsalicylic acid, Diclofenac, Fenoprofen
Psychiatric drugs	Diazepam
Anticonvulsant drugs	Carbamazepine
Lipid regulators	Benzafibrate, Clofibric acid, Fenofibric acid
β-blockers	Metoprolol, Propanolol, Timolol
X-Rey contrast agents	Iodopromide, Iopamidol, Diatrizoate,
Steroids and Hormones (contraceptives)	Estradiol, Estrone, Estriol, Diethylstilbestrol
Personal Care Products	
synthetic musk fragrances	Musk xylene, Galaxolide, Tonalide
Sun-screen agents	Benzophenone, Methylbenzylidene camphor
Insect repellents	N,N-diethyltoluamide
Surfactants and metabolites	Alkylphenol ethoxylates, Alkylphenoles (Octylphenol, Nonylphenol), Alkylphenol carboxylates
Flame retardants	Polybrominated diphenylethers (PBDEs), Tetrabromo bisphenol A, Tris-(2-chloroethyl)phosphate
Industrial additives and agents	Chelating agents (EDTA), aromatic sulfonates, benzotriazole, bisphenoles, phthalates
Gasoline additives	Dialkylethers, Methyl-t-butylether (MTBE)
Disinfection by-products	Bromoacids, Iodo-THMs, Bromoacetonitriles, Cyanoformaldehyde, NDMA,
Pesticides	Carbaryl, Metolachlor, Alachlor, 2,4-D, Dieldrin, Lindane, Esfenvalerate, Simazine, Atrazine, Isoproturon

Table 1. Types of contaminants found in the environment

Factories and manufacture are the main sources of these contaminants where ECs are either every day products or used as raw materials to produce other products (Marttinen, Kettunen&Rintala, 2003; Moon et al., 2007).Wastewater treatment plants are also a well-known source. The main aim of the wastewater treatment plant is to produce treated effluent that is suitable and safe to discharge to the environment and increasingly to reuse it. Therefore, the role of wastewater treatment is to convert the waste material present in the wastewater to stable oxidized end products (Gray, 2004). Therefore STWs are assembled from a combination of unit processes. In general, there are five stages during sewage treatment:

- Preliminary treatment: gross solid and grit are removed and sometime oil and grease as well if they present in large amount.

- Primary (sedimentation) treatment: the settable solids are removed in the sedimentation tanks. Secondary (biological) treatment: in this stage, the organic matter (dissolved and colloidal) with presence of microorganisms is removed.
- Tertiary treatment: the residual suspended solid and nutrient are removed.
- Sludge treatment: sludge collected from previous stage are treated by dewatering, stabilization in order to disposal it.

Many natural and synthetic emerging contaminants from households, hospitals, industrial use, and sometimes from storm water enter the sewage treatment works. Because these contaminants are not fully or partially removed during the chemical, physical, and biological treatment processes (Gros et al.,2010; Jelic et al., 2011). A considerable amount of these ECs, like natural hormones and benzotriazoles, are released to the receiving water (Desbrow et al., 1998; Weiss &Reemtsma, 2005). In addition, in some cases (such as storm events), the untreated or partially treated wastewater may reach the receiving water and could also have significant amounts of these contaminants. Thus, wastewater treatment plants seem to be an important source of emerging contaminants (Tan et al., 2007). The impact of ECs on the environment and wild life represented by some problems in reproductive systems in fish, birds, and mammals in addition to the breakage of eggs of fish, birds and turtles, additionally feminization of male fish and finally some changes in the immunologic system of marine mammals. The ECs can influence the human also represented via reduction in sperm count and increase the incidence of breast or endometriosis cancer for women, testis and prostate cancer from men (Esplugas et al., 2007).

3. Water remediation technologies

Advanced oxidation processes (AOPs) have been identified as a promisingalternative to conventional treatment for removing a wide range of organicconstituents in contaminated water and wastewaters. Their development andapplication has been studied extensively over the last few decadesusing a variation of combined oxidants, catalysts and radiation. Some of theseinclude Fentons reagent (Fe^{2+}/ H_2O_2), ozone and hydrogen peroxide (O3/H_2O_2),UV with ozone (UV/O3), hydrogen peroxide (UV/H_2O_2) and titanium dioxide(UV/TiO_2); the more established and commercially available processes (Suty etal., 2004) utilized for water purification (drinking, wastewater and groundwater treatment). AOPs have the potential to achieve full mineralisation, or possible transformation to less potent products (Bolton, 2001), and are thus considered appropriate for drinking water and industrial applications. An AOP is typically characterised by the formation of hydroxyl radicals ($HO^{•}$) (Glaze et al., 1987) to induce the oxidation and degradation of target contaminants, predominately organic materials. .OH radicals are well known for being one of the most powerful, non-selective and short lived oxidants (Sanches et al., 2010), potentially producing a large number of reactions, suitable for multiple treatment objectives. These reactions are highly accelerated, exhibiting rate constants in the range of 10^8 –10^{10} M^{-1} s^{-1} (Murray and Parsons, 2004) – an order of magnitude faster than molecular ozone. Contaminant degradation rates are generally proportional to the rate constant for the species with $HO^{•}$radical. However, the degradation rates can be impacted by background organic compounds present in source water (Hoigne, 1988) and scavengers of .OH such as organic carbon and bicarbonate/carbonate ions (Wu and Linden, 2008). Under such circumstances complete mineralisation may only be achievable at extended treatment times and with excessive chemical usage, unlikely to be economically or practically favourable at larger scales (Wadley and Waite, 2004). The following technologies are most economically favorable and efficient.

3.1 Ultraviolet (UV) photolysis

The application of UV for disinfecting water dates back to several decades inEurope in particular. In more recent years the use of chlorine as a primarydisinfectant has started to be phased out in some regions due to its limitedability to effectively inactivate some micro-organisms, and specificallyCryptosporidium (Craik et al., 2001), without generating significant levels ofdisinfection by-products. Conventional sources of UV radiation (200-400 nm) forwater treatment comprise low pressure (LP-UV) and medium pressure (MP-UV)mercury (Hg) lamps with high and low intensities. LP lamps emit essentiallymonochromatic light at 253.7 nm, whilst MP polychromatic light sources emit inthe wavelength range of 200 – 800 nm. Apart from their difference in spectralwavelength, LP lamps offer more efficiency, consume less power and have alonger lamp life (Stefan, 2004), compared to the smaller footprint and higheroutput provided by the MP lamps. The optimal wavelength for disinfection isUV-C, or the germicidal range (200 – 280 nm), provided by both lamp types. UV light also provides a means of degrading organic matter through a directphotolysis. This can be effective for compounds that exhibit large molarabsorption coefficients and high quantum yields across the lamps emissionspectrum

(Wu and Linden, 2008). The energy associated with the molecularbonds must be lower than that absorbed from the UV photons to initiatephotolysis (Bolton, 2001). These factors must be considered in lamp selection,since the wavelength spectrum needs to be within the range of the targetpollutant. The process performance is also affected by various water qualitycomponents, such as UV transmittance (UVT), turbidity/ suspended solids andfoulants such as organic matter and iron that can precipitate onto the quartzsleeves (Linden et al., 2004). In general, the relative efficiency of UV photolysisin degrading most micropollutants is low, but in combination with a chemical oxidant their elimination rate can be greatly enhanced.

3.2 UV and hydrogen peroxide (UV/H2O2)

The UV/H2O2 process is among the most studied AOPs and has become a keypolishing step in full scale systems for wastewater reuse (Royce et al., 2010).UV-photolysis of H_2O_2 activates the formation of $HO^•$by homolytic cleavage ofthe central HO-OH bond (Clarke and Knowles, 1982; Chang and Young, 2000),yielding the formation of two $HO^•$per mole of H_2O_2.

Eq.1. $$H_2O_2 \xrightarrow{h\nu} 2\,HO^•$$

The efficiency of the reaction pathway is limited by the low molar absorptioncoefficient of H2O2 at 254 nm (19.6 M^{-1} cm^{-1}; Baxendale and Wilson, 1957),demanding a high H_2O_2 concentration to generate sufficient $HO^•$radicals.However, high concentrations of H_2O_2cause scavenging of the $HO^•$radicals,impairing the process efficacy (Wang et al., 2000).

Eq.2. $$H_2O_2 + HO^• \xrightarrow{h\nu} HO_2^• + H_2O$$

3.3 UV and ozone (UV/O3)

Ozone (O_3) has traditionally been used for disinfection and oxidation (taste andodour control, colour removal and micropollutant detoxification) in drinking watertreatment plants (Hoigne, 1988; von Gunten, 2003).However, it is a selective oxidant compared to $HO^•$, and the production of $HO^•$radicals via O_3 decomposition is relatively low. Combining ozone with UVirradiation, H_2O_2, or both, enhances $HO^•$generation.The photolysis of O_3 by UV leads to the formation of H_2O_2 and O_2, wherebyH2O2 reacts further with O_3 to produce the $HO^{\bullet}$radical (Bolton, 2001).

Eq.3. $$O_3 + H_2O \xrightarrow{h\nu} H_2O_2 + O_2$$

Eq.4. $$O_3 + H_2O_2 \xrightarrow{h\nu} HO^{\bullet} + HO_2^{\bullet} + O_2$$

Eq.5. $$H_2O_2 \xrightarrow{h\nu} 2\,HO^{\bullet}$$

This process can be extremely effective because of its high oxidation potentialas a result of the high molar absorption coefficient at 254 nm of O_3 (3301 $M^{-1}cm^{-1}$) as well as contaminants being exposed to bothoxidants. The production of O_3 incurs relatively high capital and operationalcosts, and ozonation also leads to the generation of bromate (a carcinogenicDBP) in waters containing bromide (IJpelaar et al., 2002). Nonetheless, thisparticular process has been extensively applied to groundwater treatment(Collivignarelli and Sorlini, 2004).

3.4 UV and titanium dioxide (UV/TiO2)

Although one of the least established and commercially developed AOPs forfull-scale treatment, UV/TiO_2 has been demonstrated at bench scale todecompose natural organic matter (NOM) (Huang et al., 2008) as well as providing disinfection (Pablos et al., 2013). The process doesnot require any chemical addition to produce .OH radicals, which are generatedby virtue of the semiconductor properties of the TiO_2. TiO_2 acts as aphotocatalyst when exposed to UV at irridation wavelengths less than 380 nm(Tran et al., 2009). Energetically excited electrons transfer from valence to theconductance band, thereby creating highly reactive charged holes – at anoxidation potential higher than fluorine – and subsequently $HO^{\bullet}$ radicals.Compounds are either directly oxidised in solution or degraded on the surfaceof the TiO_2 particle.Using TiO_2 has several advantages in that it is relatively inexpensive toproduce, is largely inert and not harmful to the environment. Additionally, thephotocatalyst process can be powered by a renewable energy source using natural solar radiation, although this source of UV light is limited in the UV-Awavelength radiation required for photoactivation of the catalyst (Ljubas, 2005).There are also engineering issues surrounding the separation of the TiO_2 fromthe treated water.

Conclusion

AOPs have been proven to eradicate a wide range of trace organicmicropollutants in various water matrices. UV/H_2O_2 and UV/O_3 provide the mostestablished technologies and have been applied at full scale for drinking waterand wastewater reclamation. Heterogeneous photocatalytic processes, such asUV/TiO_2, are attracting increasing attention because of their potential to bepowered by renewable energy sources (i.e. solar irradiation) as well as using low cost consumables. However, there remain several engineering challengesthat require further development before full-scale implementation. MP removalefficiency is shown to be impacted by the presence of inorganic compounds(bicarbonate/ carbonate) and NOM in the treated water.The theory, kinetics and mechanisms behind photo-oxidation are generally wellunderstood (Crittenden et al., 1999). Thus, the present research is raising awareness on the concern of emerging contaminants in the republic of Djibouti. One area ofultimate concern is the chemical nature (and specifically toxicity) and extent offormation of degradation by-products (including biodegradable organics). Eventhough literature data exists on this issue, there remains a paucity of knowledgerelating to pharmaceutical and PPCP by-products in particular.

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