PHYSICO-CHEMICAL PROCESSES FOR ORGANIC REMOVAL FROM WASTEWATER EFFLUENT

H.K. Shon, S. Phuntsho, S. Vigneswaran and J. Kandasamy
Faculty of Engineering, University of Technology, Sydney, Australia

J. Cho
NOM Ecology Lab., Gwangju Institute of Science and Technology, Gwangju, Korea

J. H. Kim
School of Applied Chemical Engineering & The Research Institute for Catalysis, Chonnam National University, Gwangju 500-757, Korea

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This chapter covers physio-chemical processes including advanced oxidation processes for wastewater treatment. The approach used in this chapter is to first provide a brief introduction to each of the processes followed by a brief description of the process fundamentals in removing organic matter. The removal of effluent organic matter (EfOM) in terms of dissolved organic carbon (DOC), molecular weight distribution (MWD) for each process is then explained followed by removal of endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs) by each process.

1. Introduction

The physico-chemical method of wastewater treatment involves either physical process or chemical process or at many times a combination of both these processes. Although their basic principles are quite different, the processes are sometimes hard to distinguish as the two processes may occur simultaneously in a single treatment unit. Sometimes the physical entrainment of organic micro pollutants in water and wastewater is also associated with biological degradation depending on the treatment environment. The sorption (definition included in the following section) of micro pollutants onto solids and, accordingly, their behaviour during the physico-chemical treatment, depends basically on their physico-chemical properties, such as lipophilicity or acidity (Carballa et al., 2005). Two types of coefficients (K_{ow}: octanol-water partition coefficient) and (K_{oc}: organic carbon partition coefficient) are usually used to determine the sorption effectiveness and the affinity of a given substance to effluent organic matter (EfOM).
However some limitations for its applicability in endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs) have been reported (Holbrook et al., 2004) and another indicator known as solid–water distribution coefficient (Kd), defined as the ratio between the concentrations of a substance in the solid and in the aqueous phase at equilibrium conditions have also been sometimes used as a suitable parameter (Ternes et al., 2004).

This coefficient takes into account the two main sorption mechanisms: absorption (hydrophobic interactions characterized by the Kow value) and adsorption (electrostatic interactions related to the tendency of the substance to be ionized or dissociated in aqueous phase, which is characterized by the dissociation constant, pKa). According to their physico-chemical properties, EDCs/PPCPs can be divided into three main groups: lipophilic (with high Kow values), neutral (non-ionic) and acidic (hydrophilic and ionic) compounds (Carballa et al., 2005).

At sewage treatment facilities, the wastewater is subjected to various treatment regimes (depending on the size and sophistication of the treatment plant), resulting in "removals" of PPCPs that range from nearly complete to nearly zero. Although the removal efficiencies are a function of the individual EDC/PPCP properties as well as the treatment process(es), their removal is also essentially a collateral or incidental function of a sewage treatment plant, as these facilities were never specifically designed to remove exotic, bioactive xenobiotics (Daughton, 2007).

In the following sections the physicochemical processes such as coagulation-flocculation, adsorption, biofiltration, ion exchange (IX) and advanced oxidation processes (AOPs) have been reviewed for their roles in removing dissolved organic matter, molecular weight distribution and EDCs and PPCPs.

2. Overview of Physico-Chemical Processes

One of the main reasons for applying physico-chemical processes in the advanced treatment of biologically treated sewage effluent (BTSE) is to remove particulate organic matter (> 0.45 µm) and dissolved organic matter (DOC < 0.45 µm). EfOM removal can be shown in terms of DOC, MWD, fraction and EDCs/PPCPs. DOC presents a surrogate for general organic contaminant removal by physico-chemical processes, MWD provides specific removal of different organic sizes, fraction represents removal of different hydrophobic/philic fractions and removal of EDCs and PPCPs can be used as an indicator for the smallest MW compounds (about 150 – 500 Da). The four parameters provide a better understanding of organic removal by physico-chemical processes.

The effectiveness of specific processes in treating EfOM is strongly influenced by the size (or MW) and structure of EfOM. The size ranges of EfOM removed by different treatment methods are shown in Figure 1. In general, flocculation and biofiltration remove the majority of particulate organic matter. Adsorption, IX and AOPs remove the small size of EfOM.
Figure 1 Size ranges of the applied treatments in treating EfOM

2.1 DOC Removal by Physico-Chemical Processes

Figure 2 shows the removal of EfOM from the same BTSE by different physico-chemical treatment at an optimum condition (Shon et al., 2006). The DOC removal depends significantly on the treatment processes used. Powdered activated carbon (PAC) adsorption and granular activated carbon (GAC) biofiltration result in relatively high DOC removal of EfOM in comparison to that of flocculation, IX and AOPs. This suggests that the EfOM consists mainly of small MW organic matter in the BTSE used.

Figure 3 shows the removal efficiency of EfOM from BTSE with chemical coupling. As expected, the removal increases significantly with chemical coupling. Enhanced removal was observed especially when coupling PAC adsorption with MIEX and PAC adsorption with flocculation which may be due to removal of different range MW by each process.
Figure 2 DOC removal by different physico-chemical processes (FeCl₃ flocculation, powdered activated carbon (PAC) adsorption, IX with magnetic ion exchange resin (MIEX®), AOPs (photocatalysis) with TiO₂, granular activated carbon (GAC) biofiltration) in BTSE from a wastewater treatment plant

Figure 3 DOC removals from BTSE with different chemical couplings

2.2 MWD Removal by Physico-Chemical Processes

MWD of EfOM is very important in understanding the removal of micropollutants under different sizes by different treatment methods. Figure 4 shows the MWD of EfOM following treatment by different physical-chemical processes. The MWD of EfOM in the BTSE used is comprised of small (260 Da, 580 and 870) and large (43100 Da) MW compounds.

The organic concentration of biopolymers, humic substances, low MW acids and low MW neutrals including amphiphilic in BTSE was 0.7 mg/L (6% content), 6.3 mg/L (53%), 2.3 mg/L (20%) and 2.5 mg/L (21%), respectively (Haberkamp et al., 2007). Flocculation removed mainly the large MW compounds and did not remove the majority of small MW (263 Da, 330 and 580) while adsorption mainly removed the small MW compounds.

The five general MW peaks in BTSE are found in i) 30 kDa – 50 kDa, ii) 1500 Da – 800 Da, iii) 800 - 500 Da, iv) 250 Da and v) < 250 Da. The compounds in the range of 30 kDa – 50 kDa are biopolymers; 1500 Da – 800 Da are humic substances; 800 - 500 Da are building blocks; 250 Da are acids, and less than 200 Da are low MW neutrals and amphiphilics (Huber, 1998).
Here, biopolymers include polysaccharides and proteins; building blocks include hydrolysates of humic substances; acids include all free mono- and diprotic low-molar-mass organic acids; low MW neutrals and amphiphilics (slightly hydrophobic compounds) include sugars, alcohols, aldehydes, ketones and amino acids.

Figure 4 MWD of the influent BTSE and effluents from different physico-chemical treatments (flocculation, adsorption, GAC biofiltration, photocatalysis, and IX with MIEX®)
2.3 Fraction Removal by Physico-Chemical Processes

Removal of different organic fractions is also helpful in determining the efficiency of different physical-chemical treatments in removing hydrophobic (HP), transphilic (TP) and hydrophilic (HL) fractions (Table 1). FeCl₃ flocculation removed a higher amount of HL fraction. This is probably due to the ionic effects of EfOM. Flocculation removes HL fraction when the pollutants are more negatively charged. In general, flocculation and adsorption are used mainly to remove the HP fraction of large and small MW organics. The removal of HL by flocculation (in this case) may be due to the large dose of FeCl₃ used (through sweep flocculation mechanism) (Shon et al., 2005). The removal of HL by adsorption could be attributed to the physical affinity between HL organic molecules and PAC (through Vander Waals, electrostatic forces and chemisorption) (Shon et al., 2004). Ion exchange with MIEX® also exhibited very high removal of hydrophilic compounds (Zhang et al., 2005).

Table 1 Efficiency of different physico-chemical treatment processes in the removal of different fractions from BTSE

<table>
<thead>
<tr>
<th></th>
<th>Initial (mg/L)</th>
<th>MIEX® (mg/L)</th>
<th>PAC adsorption (mg/L)</th>
<th>Flocculation (mg/L)</th>
<th>Photocatalysis (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP</td>
<td>1.645</td>
<td>0.715 (56.5%)</td>
<td>0.460 (72.0%)</td>
<td>0.999 (39.3%)</td>
<td>0.802 (51.2%)</td>
</tr>
<tr>
<td>TP</td>
<td>1.034</td>
<td>0.705 (31.8%)</td>
<td>0.282 (72.7%)</td>
<td>0.802 (22.4%)</td>
<td>0.703 (32.0%)</td>
</tr>
<tr>
<td>HL</td>
<td>3.822</td>
<td>1.180 (69.1%)</td>
<td>1.258 (67.1%)</td>
<td>1.540 (59.7%)</td>
<td>2.810 (26.5%)</td>
</tr>
</tbody>
</table>

2.4 EDCs/PPCPs Removal by Physico-Chemical Processes

It is difficult to remove EDCs and PPCPs within the range from 100 to 500 Da in EfOM. Removal of EDCs and PPCPs is thus considered as the main parameter in determining the efficiency of a particular treatment method. Considering treatments by flocculation, adsorption and oxidation, the removal of these compounds showed very different trends (Table 2). Some of them are removed by up to 90%, while the others can only be partially removed (Barceló, 2003). This suggests that removal of the emerging contaminants requires the careful selection of treatment methods depending on the individual EDC and PPCP structure and treatment application/dose.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculation</td>
<td>&gt;50% removal of: benzo[a]pyrene, benzo [g,h,l]perylene, benzo[k]fluoranthene, mirex, benzo[b]fluoranthene, benzo[a]anthracene</td>
</tr>
<tr>
<td></td>
<td>&lt;10% removal of: diazepam, diclofenac, meprobamate, sulfamethoxazole, trimethoprim</td>
</tr>
<tr>
<td>Adsorption</td>
<td>&gt;90% removal of: triclosan, fluoxetine, oxybenzone, mirex, DDT</td>
</tr>
<tr>
<td></td>
<td>&lt;50% removal: meprobamate, sulfamethoxazole, iopromide, trimethoprim, gemfibrozil</td>
</tr>
<tr>
<td>Chlorination</td>
<td>&gt;90% removal of: 17β-estradiol, oxybenzone, triclosan, sulfamethoxazole, benzo[a]anthracene</td>
</tr>
</tbody>
</table>
Table 2 Unit processes and operations used for EDCs and PPCPs removal in WWTP

<table>
<thead>
<tr>
<th>Group</th>
<th>Classification</th>
<th>AC* adsorption</th>
<th>O3/AOP</th>
<th>UV</th>
<th>Cl2/ClO2</th>
<th>Flocculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDCs</td>
<td>Pesticides</td>
<td>E</td>
<td>L-E</td>
<td>E</td>
<td>P-E</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>Industrial chemicals</td>
<td>E</td>
<td>F-G</td>
<td>E</td>
<td>P</td>
<td>P-L</td>
</tr>
<tr>
<td></td>
<td>Steroids</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>Metals</td>
<td>G</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>F-G</td>
</tr>
<tr>
<td>Inorganics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Organometallics</td>
<td>G-E</td>
<td>L-E</td>
<td>F-G</td>
<td>P-F</td>
<td>P-L</td>
</tr>
<tr>
<td>PPCPs</td>
<td>Antibiotics</td>
<td>F-G</td>
<td>L-E</td>
<td>F-G</td>
<td>P-G</td>
<td>P-L</td>
</tr>
<tr>
<td></td>
<td>Antibiotics</td>
<td>G-E</td>
<td>L-E</td>
<td>F-G</td>
<td>P-F</td>
<td>P-L</td>
</tr>
<tr>
<td></td>
<td>Anti-inflammatory</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>P-F</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>Sunscreens</td>
<td>G-E</td>
<td>L-E</td>
<td>F-G</td>
<td>P-F</td>
<td>P-L</td>
</tr>
<tr>
<td></td>
<td>Antimicrobials</td>
<td>G-E</td>
<td>L-E</td>
<td>F-G</td>
<td>P-F</td>
<td>P-L</td>
</tr>
</tbody>
</table>

*AC, activated carbon; E, excellent (>90%); G, good (70-90%); F, fair (40-70%); L, low (20-40%); P, poor (<20%)

Table 3 Anticipated physico-chemical processes and operations for EDC and PPCP removal

Table 3 presents the universal performance of different unit processes in removing typical classes of EDCs and PPCPs (Snyder et al., 2003b). In general, flocculation cannot remove the majority of EDCs/PPCPs, while activated carbon can be used to adsorb many different EDCs/PPCPs. AOPs can moderately remove specific EDCs/PPCPs. Snyder et al., (2003b) reported that dissociated acidic EDCs/PPCPs were more reactive than protonated forms, suggesting that removal of EDCs/PPCPs is pH dependent. Functional groups that affect removal are in the order of thiols > amines > hydroxyl > carboxyl. Aromatic group of EDCs/PPCPs showed better removal in comparison to aliphatic compounds.
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Biographical Sketches

**Dr H.K. Shon** is currently a UTS Chancellor’s postdoctoral research since 2006. His research interests include membrane processes and new analytical methods for wastewater treatment and reuse. He has made significant contributions to the understanding of membrane fouling in wastewater treatment processes.

**Mr Sherub Phuntsho** is an engineer working for the Department of Urban Development and Engineering under the Ministry of Works and Human Settlements, Royal Government of Bhutan, Thimphu. He heads the Urban Waste Management Section of the Urban Infrastructure Services Division. He is responsible for planning and design of any works related to urban sewerage and solid waste management system in the form of technical assistance to all the local municipal authorities in Bhutan. He recently reviewed the performance of a sewage treatment plant for Thimphu city which is soon expected to be published in a journal. He is currently working on a research to study the municipal solid waste management systems including the quality and quantity of waste generated in the urban centres of Bhutan. He is also coordinating to organize a national level conference on solid waste management 2008 in Bhutan.

**Dr S. Vigneswaran** has been working on water and wastewater treatment and reuse related research since 1976. During the last twenty years, he has made significant contributions in physico-chemical water treatment related processes such as filtration, flocculation, membrane-filtration and adsorption. His research activities both on new processes development and mathematical modeling are well documented in reputed international journals such as Water Research, American Institute of Chemical Engineers Journal, Chemical Engineering Science, Journal of American Society of Civil Engineers, and Journal of Membrane Science. He has also been involved in a number of consulting activities in this field in Australia, Indonesia, France, Korea, and Thailand through various national and international agencies. He has authored two books in this field at the invitation of CRC press, USA, and has published more than 230 papers in journals and conference's proceedings. Currently a Professor of the Environmental Engineering Group at the University of Technology, Sydney, he was the founding Head of and the founding Co-ordinator of the University Key Research Strength Program in Water and Waste Management. He is coordinating the Urban Water Cycle and Water and Environmental Management of the newly established Research Institutes on Water and Environmental Resources Management and Nano-scale Technology respectively.

**Dr J. Kandasamy** is Senior Lecturer in the Faculty of Engineering University of Technology, Sydney, Australia. He obtained his PhD from University of Auckland., New Zealand where is also obtained his Bachelor in Civil Engineering and Masters in Civil Engineering. He has worked in the New South Wales Government as a Senior Engineer for 15 years and has wide industry knowledge.

**Dr J. Cho**, associate professor at Gwangju Institute of Science and Technology, has been studying on research for water reuse using various technologies, including constructed wetland and membrane filtration. He is recently interested in research of ecological engineering as well as related education. He is an editorial board member of Journal, Water Science and Technology, IWA and newsletter editor of Water Reuse Specialty Group in IWA.

**Dr J.H Kim** is presently working at the School of Applied Chemical Engineering, Chonnam National University, and the President of Photo and Environmental Technology Ltd. His research interest is a leading expert on the photocatalyst technology using TiO2 photocatalyst to purify air and water. He was
awarded an excellent innovative business award from INNO-Biz in 2001 and gold prize for Korean New Technology from the Prime Minister of Korea in 2003. He is also Director of The Research Institute for Catalysis and Research Center for Nano-Energy Materials in Chonnam National University. He has 26