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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1002/cjce.23533>

The Canadian Journal of Chemical Engineering, 97, 10, pp. 2621-2631, 2019-09-12

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1 Advancement in Treatment of Wastewater: Fate of Emerging Contaminants

2
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7 8 **Abstract**

9 Wastewater (WW) treatment, recycle, and reuse have become important alternate sources of
10 water supply. Treating wastewater requires a comprehensive planning, design, construction, and
11 management of treatment facilities to ensure that the treated water is safe for recycle and reuse.
12 Growing population and urbanization have led to the release of many persistent emerging
13 contaminants (ECs) to environment, mainly detected in WW. The presence of ECs in the aquatic
14 environment may cause ecological risk such as interference with endocrine system of high
15 organisms, microbiological resistance, and accumulation in soil and plants, as these ECs are not
16 completely removed by conventional wastewater treatment processes. The biggest problem with
17 these compounds is their detection (ng or pg level) mainly in media with complex matrices, such
18 as WW samples. The purpose of this review is to provide information on advancement in
19 wastewater treatment technologies such as constructed wetland (CW) and advanced oxidation
20 processes (AOPs) and the fate of emerging contaminants during these treatments. Further, this
21 review also reports the ecological effects of these contaminants and their by-products formed
22 during various treatment processes of wastewater. The review also discusses the advancement in
23 different analytical techniques for emerging contaminants analysis in wastewater.

24 **Keywords:** Advanced treatment; Analytical techniques; Emerging contaminants; Mass balance;
25 Toxicity; Wastewater

26

27 **1. Introduction**

28 Effective reclamation and re-use of wastewater (WW) have received less attention in
29 comparison to water supply and treatment. However, in the last decade, fresh water supply
30 scarcity has shifted the focus of water to consider the importance of WW re-use, recycle and
31 reclamation through new and advanced treatment in policy making in both developed and
32 developing countries. As urban water scarcity is growing and water purification technology is
33 advancing, WW is increasingly reclaimed and recycled for both urban and industrial use around
34 the world (Levine and Asano, 2004). Dependence on the fresh water source and severe water
35 pollution is also intensified by the sudden increase in urbanization through population expansion,
36 fast industrialization, and climate change. One of the main sources of freshwater pollution is
37 attributed to the generation of the huge volume of toxic contaminants in industrial waste and
38 dumping of industrial effluents. There is also an increasing demand for clean water particularly
39 in water-stressed areas due to the rapid growth in population and economy (Xiao et al. 2015).
40 The development of advanced and cost-effective treatment approaches is desired for treatment of
41 WW and recovery of water resources.

42 The presence of xenobiotics, such as endocrine disruptor compounds (EDCs), pharmaceuticals
43 and personal care products (PPCPs), pesticides, and various industrial additives among others in
44 the environment has raised concerns about the impact of these emerging contaminants (ECs) on
45 the environment and on public health. Generally, these are referred to as ECs due to their recent
46 identification, the frequency of occurrence or sources may not be known and as they have been
47 linked to human health and/or environmental risks. These newly recognized contaminants

48 represent a shift in traditional thinking as many are produced industrially yet are dispersed to the
49 environment from domestic, commercial, and industrial uses.

50 The potential deleterious effects associated with the presence of ECs in WW and further
51 release to surface waters have been reported to result in reduction of macroinvertebrate diversity
52 in rivers (Kuzmanović et al. 2016), affect fish population (Yeh et al. 2017) as well as cause
53 physiological stress in freshwater mussels (Oliveira et al. 2017). In addition, the current available
54 knowledge is insufficient to allow proposing ways to control the release of ECs into the
55 environment due to lack of information about the contaminant sources. Most of the ECs are
56 persistent and difficult to biodegrade. In order to protect the water resources from such
57 contaminants following options should be considered such as: (i) determination of the source of
58 ECs; (ii) assessing effects: studying the nature and toxicity of ECs and its by-products that
59 formed during different treatment of WW; (iii) WW treatment: developing/improving treatment
60 technologies for WW treatment to mitigate the release and impacts of ECs; and (iv) assessing
61 exposure: performing environmental assessment to evaluate the discharges of ECs into the
62 environment and the potential for WW and WWS treatment to mitigate environmental impacts.

63 Since, conventional wastewater treatment plants (WWTPs) are not designed for the treatment
64 of ECs, their eventual discharge into fresh water results in many of these compounds occur at
65 different concentrations in natural water bodies. Recognizing this limitation, advancements in
66 WW treatment technologies have led to a suite of treatment technologies to provide advanced
67 wastewater treatment to enable better end-use application of the treated effluents and WWS and
68 comply with new stringent discharge regulations. Advancement in WW treatment technologies
69 includes; sand and media filtration, adsorption using granular activated carbon, zeolite or other
70 clay materials, membrane bioreactors, biological treatment, chlorination, hydrolysis, and an

71 emerging suite of advanced oxidation processes (AOPs), which can be applied based on the
72 treated effluent quality requirements and matching specific end-uses (Mohapatra et al. 2014).
73 Different AOPs such as ultrasonication, Fenton's oxidation, ozonation, photolysis, photo-Fenton,
74 photocatalysis, solar driven processes, and electro-Fenton process has been used for the removal
75 of ECs from WW. Furthermore, some hybrid systems have recently been applied to enhance the
76 removal of a wide range of ECs from WW.

77 However, assessing the occurrence, distribution, reactivity, effects of emerging contaminants
78 in the environment and effect of a range of proposed treatment methods for the removal of these
79 contaminants from complex matrices such as WW remains major time- and resource-intensive
80 challenges. Therefore, it is necessary to study the fate of ECs during or after pre-treatment of
81 WW and secure an innovative practice for discharge of WW to river and sludge recycling and
82 reuse. The purpose of this review is to provide information on advancement in wastewater
83 treatment technologies such as constructed wetland and advanced oxidation processes and the
84 fate of emerging contaminants during these treatments. Further, this review also reports the
85 ecological effects of these contaminants and their by-products formed during various treatment
86 processes of wastewater. The review also discusses the advancement in different analytical
87 techniques for emerging contaminants analysis in wastewater.

88 **2. Advancement in wastewater treatment for emerging contaminants removal**

89 Conventional municipal wastewater treatment plants are not designed for the removal of
90 micropollutants such EDCs, PPCPs, pesticides, detergents and various industrial additives
91 among others at mg/L and $\mu\text{g/L}$ levels. As a consequence, these pollutants end up in the
92 environment and may result in a multitude of risks to all living organisms like bacterial
93 resistance, feminization of aquatic organisms, neurotoxicity, endocrine disruption and cancer. To
94 develop treatment solutions for EC's, different constructed wetland systems such as free water

95 surface, horizontal subsurface flow, and vertical subsurface flow constructed wetland have been
96 designed to remove ECs from WW. Constructed wetland (CW) based WW treatment is achieved
97 by interactions among plants, substrate and soil via synergistic processes that include hydrolysis,
98 volatilization, sorption, biodegradation, and photolysis (Wang et al. 2017). Matamoros et al.
99 (2017) studied the capacity of horizontal-flow constructed wetlands (HFCWs) used as tertiary
100 treatment to remove ECs from secondary treated WW. They observed 43% average removal of
101 ECs from WW. Further, they concluded that HFCWs are suitable for removing ECs from
102 WWTP effluents and, therefore, reduce the eco-toxicological effects associated with pollutant
103 discharges. Constructed wetland technology can be successfully applied for small communities
104 for the remediation of a wide range of ECs but it will be difficult to use it in large cities due to
105 the lack of space to perform such wastewater treatment processes.

106 Emerging contaminants removal by using a full-scale hybrid constructed wetland system for
107 WW reuse was studied by Avila et al. (2015). They reported a higher rate of removal (>80%) of
108 ECs such as EDCs and PPCPs from WW due to the combination of physico-chemical methods
109 leading to abiotic/biotic removal mechanisms to occur such as photodegradation, biodegradation,
110 sorption, volatilization, and hydrolysis. Impact of hydraulic and carbon loading rates of
111 constructed wetland on removal of ECs from WW was studied by Sharif et al. (2014). They
112 suggested that without increasing the cumulative hydraulic loading rates, operating two wetlands
113 in series with varying carbon loading rates could be a way to improve ECs removal from WW.
114 Further, a study by Matamoros et al. (2008) on removal of PPCPs from secondary effluent by
115 using a full-scale surface flow constructed wetland showed 90% removal efficiencies and they
116 concluded that the higher removal efficiency was due to the high hydraulic retention time (HRT).
117 Park et al. (2009) studied the effective control of ECs by using an engineered constructed

118 wetland connected to both a WWTP and a river. They observed higher removal trends for
119 atenolol, naproxen and triclosan and medium-range and low removal behaviors for
120 sulfamethoxazole, dilantine, carbamazepine, diazepam and triclosan. Further, Avila et al. (2015)
121 studied the removal of ECs from WW by using a hybrid constructed wetland system (two
122 vertical flow, one horizontal flow and one surface flow CW in series) under different hydraulic
123 loading rates. They reported that the use of hybrid CW systems is a suitable wastewater
124 treatment technology for removing ECs and reducing the toxicological effects even at high
125 hydraulic loading rates. A review on efficiency of CWs (by considering configuration design,
126 hydraulic mode, temperature and seasonality, pH, oxygen and redox potential parameters) for
127 removing pharmaceuticals from WW was reported by Li et al. (2014). They reported most
128 studies on CW were undertaken at a microcosm-scale or mesocosm-scale and further suggested
129 more research work on novel constructed wetlands such as the tidal flow constructed wetlands,
130 anti-sized constructed wetlands, and the dewatered alum sludge based constructed wetlands.

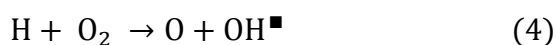
131 Further, AOPs have emerged as an important class of technologies for the oxidation and
132 destruction of wide range of organic pollutants from WW and WWS. AOPs involve in situ
133 generation of highly reactive species, such as the hydroxyl radical (OH^\bullet), which is non-selective
134 in nature and thus readily attacks a large group of organic chemicals to either totally mineralize
135 them or convert them to less complex products. Over the past 30 years, research and
136 development concerning AOPs has been immense particularly for two reasons, such as the
137 diversity of the technologies involved and the areas of potential application. Different AOP
138 methods include heterogeneous and homogenous photocatalysis based on near ultraviolet (UV)
139 or solar visible irradiation, electrolysis, ozonation, ultrasonication (US), Fenton's reagent, and
140 wet air oxidation (WAO), while less conventional but evolving processes include ionizing

141 radiation, microwaves, pulsed plasma and the ferrate reagent. Different essential parameters that
142 should be taken consideration during AOPs are solution temperature, concentrations of initial
143 pollutant and catalyst, initial pH, dosages of Fenton's reagent and hydrogen peroxide (H_2O_2),
144 ultrasonic power density, gas sparging, addition of radical scavenger, addition of carbon
145 tetrachloride and methanol among others.

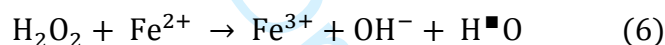
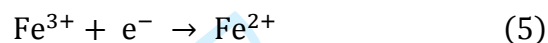
146 Sonochemistry refers to the chemical effects generated by ultrasound and the resulting
147 phenomenon in aqueous media is acoustic cavitation. Acoustic cavitation has been widely used
148 for the treatment of wastewater to enhance chemical reaction rate and facilitate the removal of
149 several pollutants. Ultrasonication processes induces acoustic cavitation into liquid media,
150 involving the generation, expansion, oscillations, splitting and implosions of numerous tiny gas
151 bubbles called cavitation bubbles. As a result of implosion of cavitation bubbles, extreme
152 temperature and pressure is generated in the centre of the collapsed bubble leading to solute
153 thermolysis as well as the formation of hydroxyl radical and hydrogen peroxide. The pyrolysis in
154 the cavitation bubbles and the generated oxidizing free radicals are responsible for the
155 degradation of polar organic compounds. Further, among the many AOPs, the Fenton process
156 has been proven to be effective for treating recalcitrant organic compounds by using Fe^{2+} and
157 H_2O_2 to produce the OH radicals. Further, recent innovation in Fenton process application have
158 led to the engineering of Fluidized-bed Fenton (FBF) process for wastewater treatment with the
159 advantage of carriers that reduce the production of sludge by crystallizing the target pollutant
160 onto the carrier surface. Further, ozonation is one of the most widely investigated techniques of
161 AOPs due to its commonly used in large number of water and WW treatment plants as a
162 clarifying and disinfecting agent. Ozonation process involves direct reaction of ECs with ozone
163 molecules through the action of secondary oxidants such as hydroxyl radicals produced from

164 ozone in aqueous solution. The degradation of ECs during different catalytic oxidation processes
 165 followed different stages such as: (i) ECs adsorbed onto the surface of the catalyst and react with
 166 hydroxyl radicals; (ii) ECs adsorbed onto the surface of catalyst and/or react with surface-bonded
 167 radicals on catalyst; and (iii) hydrogen peroxide degradation process.

168 Ultrasonic process:



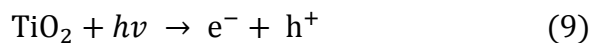
169 Fenton process:



170 Ozonation process:



171 Photocatalysis process:



172 Mohapatra et al. (2011) compared ultrasonication, Fenton oxidation and combined ferro-
 173 sonication processes for degradation of bisphenol A (BPA), an endocrine disruptor from sewage
 174 water. They reported higher suspended solids (SS), volatile suspended solids (VSS), chemical
 175 oxygen demand (COD) and soluble organic carbon (SOC) solubilization (39.7%, 51.2%, 64.5%
 176 and 17.6%, respectively) during combined ferro-sonication pre-treatment process carried out for
 177 180 min, resulting in higher degradation of BPA (82.7%). Pulicharla et al. (2017) compared three

178 different AOPs such as ultrasonication, Fenton's oxidation and combined, ferro-sonication
179 processes for degradation of chlortetracycline (CTC), an antibiotic of tetracyclines (TCs) family
180 and most commonly used in veterinary infections, from WWS. They reported higher degradation
181 efficiency (>82%) during combined ultrasonication and Fenton oxidation treatment due to higher
182 generation of OH radicals in medium, and further utilization of iron to generate more OH
183 radicals in sludge. Further, a comparative study of ultrasonication, Fenton's oxidation and ferro-
184 sonication (combination of ultrasonication and Fenton's oxidation) process for degradation of
185 carbamazepine (CBZ) from WW was studied by Mohapatra et al. (2013). They reported higher
186 soluble chemical oxygen demand (SCOD) and soluble organic carbon (SOC) increment (63 to
187 86% and 21 to 34%, respectively) was observed during Fenton oxidation pre-treatment process,
188 resulting in higher removal of CBZ (84 to 100%) from WW. Wang and Bai (2017) reviewed
189 heterogeneous catalytic ozonation of ECs (pharmaceuticals, phthalic acid esters, pesticides and
190 herbicides, dyes, nitrobenzenes, and phenols) in WW by utilizing Fe-based catalysts (Fe⁰-
191 derived, FeOOH-derived, Fe₂O₃-derived, Fe₃O₄-derived and iron oxides composite). They
192 reported higher efficiency of these Fe-based catalysts for ECs removal from WW, however
193 suggested the combination of these catalytic processes with other processes such as ultraviolet,
194 ultrasound, biological aerated filter among others to enhance the mineralization of organic
195 contaminants. Further, Sun et al. (2017) compared five different advanced treatment processes
196 such as coagulation sedimentation, nan da magnetic polyacrylic (NDAP) anion exchange resin
197 adsorption, activated carbon adsorption, ozonation and electro-adsorption in removing endocrine
198 disruption effects from municipal wastewater secondary effluent. They reported that all the
199 advanced oxidation treatment options tried are efficient for the removal of endocrine disruption
200 effects from WW. Removal of ECs from WW by application of ozone at a pilot-plant scale was

201 investigated by Ibanez et al. 2013. They reported that ozone treatment as a highly efficient
202 process for significantly decreasing the concentrations of most of the ECs present in WW.
203 Degradation of BPA during sewage solubilisation by ozonation treatment was studied by
204 Mohapatra et al. (2012a). They reported that among all the treatment parameters studied, ozone
205 dose had more significantly (probability (p)<0.001) affected the efficiency of the ozonation
206 treatment by increasing sludge solids (suspended solids (SS) and volatile solids) solubilization
207 and organic matter (soluble chemical oxygen demand and soluble organic carbon) increment and
208 BPA degradation from sewage water.

209 Further, a developing approach has been considered by use of electrochemical oxidation
210 process using boron-doped diamond anodes as an AOP process for the formation of physically
211 adsorbed hydroxyl radicals for complete and non-selective degradation of ECs from WW.
212 Comparison of Fenton oxidation and conductive-diamond electro-oxidation for treatment of real
213 effluents from the pharmaceutical industry was carried out by Perez et al. (2017). They
214 concluded that conductive-diamond electro-oxidation process as more efficient (higher removal
215 of pharmaceutical compounds in 80% of samples) as compared to Fenton process and further
216 reported that the mean oxidation state of carbon can serve as a benchmarking parameter to
217 understand the behavior of different oxidation technologies. Zheng et al. (2016) used three-
218 dimensional electrochemical oxidation process for the advanced treatment of wet-spun acrylic
219 fiber manufacturing WW. They reported that the three-dimensional electrochemical oxidation
220 process remarkably improved the treatment efficiencies for chemical oxygen demand (COD),
221 NH₃-N, total organic carbon (TOC), and ultraviolet absorption at 254 nm (UV₂₅₄) by 44.5%,
222 38.8%, 27.2%, and 10.9%, respectively. Comparison of different electrochemical advanced
223 oxidation processes such as anodic oxidation (AO), anodic oxidation with electrogenerated H₂O₂

224 (AO-H₂O₂), electro-Fenton (EF), photoelectro-Fenton (PEF) and solar photoelectro-Fenton
225 (SPEF), alone and in combination with other methods like biological treatment,
226 electrocoagulation, coagulation and membrane filtration processes was reported by Moreira et al.
227 (2017). They reported the ability of different treatment methods to oxidize the various types of
228 wastewaters can be arranged in the order: SPEF > PEF > EF > AO-H₂O₂ ≈ AO. Further,
229 photoelectrocatalytic oxidation processes combining both photocatalytic and electrolytic
230 processes have been evolved as an efficient technique for the removal of ECs from WW.
231 Removal of CTC from spiked municipal WW using a photoelectrocatalytic process operated
232 under sunlight irradiations was studied by Daghrir et al. (2014). They reported degradation of
233 99% of CTC during photoelectrocatalytic process operated at 0.6 A of current intensity with 180
234 min of treatment time. Carbamazepine degradation in WW by using photocatalytic
235 nanocrystalline TiO₂ and ZnO was reported by Mohapatra et al. (2014). Higher photocatalytic
236 degradation of carbamazepine was observed (100%) by using whey stabilized TiO₂ nanoparticles
237 with 55 min irradiation time as compared to ZnO nanoparticles (92%). Further, they concluded
238 that the higher degradation of CBZ in WW by using TiO₂ nanoparticles as compared to ZnO
239 nanoparticles was due to formation of higher photo-generated holes with high oxidizing power of
240 TiO₂. Further, Guedes et al. (2015) studied the feasibility of electro-dialytic process for removal
241 of six ECs (bisphenol A, ibuprofen, 17β-oestradiol, 17α-ethinyloestradiol, caffeine, and
242 oxybenzone) from WWS. They reported that electro degradation of ECs in WWS medium
243 enhanced changes in the microbial community, leading to higher remediation potential of the
244 medium.

245 Klancar et al. (2016) studied the application of various electrode materials, including mixed
246 metal oxide, platinum electrode, boron-doped diamond, and high voltage sparks for WW

247 treatment to reduce the ecological burden from pharmacotherapy ((bisoprolol, carbamazepine,
248 ciprofloxacin, clofibrac acid, diclofenac, fluoxetine, imatinib and metoprolol)) and the
249 agricultural use of pesticides (atrazine, simazine). They reported higher degradation efficiency of
250 >85% showed by boron-doped diamond and mixed metal oxide electrodes in 60 min of treatment
251 for the majority of the compounds as compared to platinum and high voltage sparks electrode.
252 They also referred this technology as a viable and feasible option to upgrade existing WWTPs in
253 order to achieve a significantly greater removal of these target pollutants, and to lessen the
254 ecological burden.

255 The hydrogen production from WW is a promising way of treating WW and producing
256 renewable energy. The hydrogen productions from biological processes such as direct and
257 indirect photolysis, photo and dark fermentation and microbial electrolysis cell (MEC) using
258 renewable resources are gaining significant attention due to reduced catalytic cost and process
259 energy demands. Khan et al. (2017) reviewed the status of MEC as a mean for hydrogen
260 production and urban wastewater treatment method. They reported that an estimated total
261 electricity of 612 and 767 MW can be produced for the years 2025 and 2035 from the domestic
262 and industrial wastewater by using MEC technology. Nanotechnology applications can be used
263 for filtering low quality waters, allowing under given conditions, the removal of salts and other
264 micropollutants from these waters. Bethi et al. (2016) reviewed nanomaterials-based individual
265 and hybrid advanced oxidation processes for treatment of wastewater. Nanomaterials assisted
266 oxidation processes may become applicable on an industrial scale when every effectiveness
267 factor is optimized and different processes are combined (hybrid system) to eliminate some of
268 the drawbacks associated with the individual techniques to achieve maximum efficiency with
269 minimum energy input. Photocatalytic degradation of ECs (caffeine and salicylic acid) by using

270 titania nanotubes was studied by Arfanis et al. (2017). They reported that titanium dioxide
271 nanotubular films after calcination at 450 °C formed anatase crystal structure, showed significant
272 photocatalytic activity with high degradation rates for both examined ECs. The characteristics of
273 the investigated WW itself exerted magnitudinal effect on the final efficiency of AOPs, therefore
274 sometimes it is difficult to compare the results reported by different researchers to make a
275 comparison of AOPs. However, further studies need to be performed in order to evaluate the best
276 effective treatment process with more cost-benefit, and to investigate the influence of operating
277 conditions and the toxicity of effluents after treatment as well.

278 **3. Mass balance and elimination efficiency of treatment plant for emerging contaminants**

279 Accurate determination of the fate of contaminants during wastewater treatment is required in
280 order to facilitate risk assessments and to identify strategies to improve their removal. The
281 elimination efficiency of particular contaminants in each specific unit of treatment plant can be
282 calculated based on the difference between total mass flux entering (M_{in}) and leaving (M_{eff}) in
283 each unit as shown in Eq.11:

$$284 \text{ Elimination Efficiency (\%)} = \frac{(M_{in} - M_{eff})}{M_{in}} \times 100 \quad (11)$$

285 In order to investigate how various treatments affect the contaminant removal and the probability
286 of formation of any treatment related products, mass balance of the target compounds should
287 be performed throughout the entire process of WW treatment. Heidler and Halden (2007) studied
288 the mass balance of triclosan during a conventional sewage treatment. They reported that among
289 the total mass of triclosan (3240 ± 1860 g/d) that entered to the treatment plant, only $50 \pm 19\%$
290 (1640 ± 610 g/d) remained detectable in WWS and less than half of the total mass ($48 \pm 19\%$)
291 was bio-transformed or lost to other mechanisms. Further, mass balance of six glucocorticoids
(prednisone, prednisolone, cortisone, cortisol, dexamethasone, and 6R-methylprednisolone) in

292 WWTP was carried out by Chang et al. 2007. They reported a higher removal (92 to 100%) of
293 most of the glucocorticoids except prednisolone (66 to 90%) in WWTPs and mention that
294 biodegradation and sorption to sludge as the key factor for the removal of glucocorticoids from
295 WWTPs. A study by Yan et al. (2014) on mass balance of pharmaceutically active compounds in
296 the largest municipal WWTP in Southwest China concluded that biodegradation as the main
297 predominant removal mechanism followed by sorption onto sludge as a relevant removal
298 pathway for most of the target compounds. To determine fate of pharmaceuticals and triclosan in
299 WWTPs, Petrie et al. (2014) carried out a mass balance study by analyzing the target compounds
300 in both aqueous and particulate phases. To establish the fate of contaminants in WWTPs through
301 mass balance, they considered three pathways such as (i) biological degradation, (ii) sorption
302 onto activated sludge, and (iii) resistance to removal from the aqueous phase. They
303 recommended to incorporate more particulate phase analysis into routine pharmaceutical analysis
304 to accurately report their concentration and to better understand their fate.

305 Further, Blair et al. (2015) evaluate the sorption and negative mass balances of
306 pharmaceuticals and personal care products during WW treatment. In this study they showed
307 negative mass balances (the sum of the soluble and sorbed concentrations increased over time) of
308 pharmaceuticals and personal care products within an aerobic batch reactor. They also reported
309 that a subset of highly degradable pharmaceuticals and personal care products, such as
310 acetaminophen, caffeine, and metformin, stopped being degraded at notable levels within an
311 activated sludge WW treatment process. Mass balance of BPA during different WW treatment
312 processes was carried out by Guerra et al. (2015). They reported median removal efficiencies of
313 treatment processes up to 77% and mention the operational conditions that most influenced BPA
314 removal are solids retention time (SRT), hydraulic retention time (HRT), and mixed liquor

315 suspended solids (MLSS). They also reported that BPA's sorption tendency to WWS was strongly
316 influenced by HRT and degree of nitrification. Mass balance and comparison of WW effluent
317 and upstream sources on fate of ECs in a mixed-use watershed was studied by Fairbairn et al.
318 (2016). They reported that mass balances established that effluent transport dominated ECs
319 loading to the watershed and further suggested that upstream dominated ECs should be
320 monitored during high-flow events and seasons because the increased concentrations that occur
321 at these times will also represent the greatest loadings. Further, Thiebault et al. (2017)
322 determined the removal efficiency of pharmaceutically active compounds in an urban WWTP by
323 considering fate and mass balance assessment. They reported the mean mass balance of the
324 various pharmaceutically active compounds was 448.5 g/d and 26.3 g/d in influents and
325 effluents, respectively. Further, they also proposed that the removal efficiency of various
326 pharmaceutically active compounds can be assessed by regulating the removal of nitrogen and/or
327 BOD, as their removal is statistically correlated with the removal efficiency of these target
328 compounds.

329 Further to evaluate the elimination efficiency of the treatment plant, the fractionated approach
330 has to be considered to identify and quantify the mechanisms of contaminant removal at each
331 stage of treatment. The solid–water distribution coefficient (K_d) can be estimated by using Eq.
332 (12) where C_s and C_l are the concentrations of target compound in the solid phase (ng/kg) and
333 the dissolved phase (ng/l), respectively.

$$K_d = \frac{C_s}{C_l} \quad (12)$$

334 An aqueous phase removal percentage, which is based on the concentrations of contaminants in
335 the influent and the effluent of treatment plants, is often used for calculating the removal
336 efficiency in treatment plants. The sorption onto solids in the treatment plant is a relevant

337 removal pathway for certain contaminants. Thus, an aqueous phase removal percentage cannot
338 comprehensively assess the removal of contaminants in treatment plants accurately. Mass
339 balance analysis approach would be an effective way to understand the fate of contaminants in
340 treatment plant and their mass loading to the receiving environments.

341 Mohapatra et al. (2011b) studied the distribution of BPA in WW and WWS to assess the
342 endocrine activity of treated effluent discharged into the environment. They reported higher BPA
343 concentration in primary and secondary sludge solids (0.36 and 0.24 $\mu\text{g/g}$, respectively) as
344 compared to their liquid counterpart (0.27 and 0.15 $\mu\text{g/L}$, respectively) separated by
345 centrifugation. Further, they concluded that BPA was present in significant concentrations in the
346 WWTP and mostly partitioned in the solid fraction of sludge (K_d value for primary, secondary
347 and mixed sludge was 0.013, 0.015 and 0.012, respectively). Further, Sun et al. (2017) studied
348 fate and mass balance of bisphenol analogues in WWTPs in Xiamen City, China. They reported
349 the concentrations of bisphenol analogues as $\text{BPA} \gg \text{BPS} \approx \text{BPF} > \text{BPE} > \text{BPAF}$ in the influent,
350 $\text{BPA} \gg \text{BPE} > \text{BPF} \approx \text{BPAF} > \text{BPS}$ in the effluent, and $\text{BPA} \gg \text{BPF} > \text{BPAF} > \text{BPS} > \text{BPE}$ in
351 the sludge. Further, mass balance of bisphenol analogues, benzotriazoles, benzothiazoles, and
352 benzophenones in Indian sewage treatment plants was reported by Karthikraj and Kannan
353 (2017). They reported the mean removal efficiency of the treatment plant for bisphenol
354 analogues, benzotriazoles, benzothiazoles, and benzophenones was 92.2%, 71.9%, 67.4% and
355 75.3%, respectively. They also reported the mass flow of target chemicals through sludge were
356 0.001 g/d (bisphenol analogues), 0.02 g/d (benzotriazoles), 7.8 g/d (benzothiazoles), and 0.007
357 g/d (benzophenones), which were less significant in comparison to emissions through effluents.

358 Partitioning of a persistent antibiotic, chlortetracycline (CTC) and its co-relation with metals
359 during mass balance in a WWTP was reported by Puicharla et al. (2014). They reported higher

360 partitioning of CTC in WWS as compared to WW and described that chelation behavior of CTC
361 with metal ions and sorption of these CTC–metal complexes to organic matter resulted in
362 accumulation of CTC in sludge phase. Tohidi and Cai (2017) studied the fate and mass balance
363 of triclosan by comparing three different types of WW treatments and aerobic/anaerobic WWS
364 digestion processes. By considering mass balance, they reported that 13.1–30.3% of triclosan
365 was adsorbed to WWS while 60–76% of triclosan underwent biodegradation in secondary
366 treatment. They also reported that the partition behavior of triclosan was correlated to the total
367 organic carbon values of the WWS and further WWS with higher total organic carbon leading to
368 higher partition of compound to the WWS.

369 Baalbaki et al. (2016) studied the fate and mass balance of ECs using fractionated approach
370 that accounts for the residence time distribution in WWTPs that includes primary, secondary and
371 tertiary treatment steps. By considering mass balance calculations they reported 50% of the
372 removal in the primary clarifier and most substantial aqueous removal occurred during activated
373 sludge treatment (up to 99%). They also reported that the estimated $\log K_d$ values (1.40 to 3.68 in
374 primary sludge and 1.36 to 4.49 in activated sludge) showed that most ECs are not significantly
375 removed by partitioning onto sludge, with the exception of triclosan. During the mass balance
376 processes, contribution of adsorption and bio-degradation to the overall removal was estimated
377 to be the main reason for ECs elimination from WWTPs. Evaluation of effect of biological
378 degradation, sorption and mass balance for removal of ECs in a conventional activate sludge
379 WWTP was carried out by Martinez-Alcala et al. (2017). They reported a higher value of
380 sorption coefficient onto sludge for carbamazepine, diclofenac and naproxen indicating that these
381 compounds are greatly absorbed onto sludge leading to higher elimination from WWTPS.
382 Further, monitoring of ECs in the aquatic environment is progressively becoming a priority for

383 the government agencies and regulatory agencies as well as the general public due to its toxic
384 effects to flora and fauna.

385 **4. Toxicity of emerging contaminants during wastewater treatment**

386 The presence of ECs in WW has raised concerns about the impact of these contaminants on the
387 environment and on public health. To evaluate the potential threat of ECs in WW to environment
388 and human health, different factors should be consider such as: (1) characterization of the point
389 as well as non-point sources of ECs that determine contaminant release to the environment, (2)
390 development of advanced analytical methods to quantify ECs and their intermediate products in
391 a variety of matrices mainly in complex matrices such as WW and WWS in trace levels, (3)
392 determination of the environmental fate and occurrence of these potential contaminants, (4)
393 define and quantify processes that determine their transport and fate through the environment,
394 and (5) identification of potential ecologic effects from exposure to ECs.

395 The identification and quantification of ECs in WW is of major interest to assess the toxicity of
396 treated effluent discharged into the environment. Eljarrat and Barcelo (2003) established priority
397 list of ECs such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins
398 (PCDDs), polychlorinated naphthalenes (PCNs), polychlorinated biphenyls (PCBs),
399 polychlorinated dibenzofurans (PCDFs), and polybrominated diphenyl ethers (PBDEs) based on
400 their relative toxic potency in environmental samples. They reported most important contributory
401 pollutants (total dioxin-like activity) in WW and WWS samples are contributed as
402 PAHs>PCNs>PCDDs/PCDFs>PCBs>PBDEs. Mohapatra et al. (2013) carried out toxicity test
403 by using yeast estrogen screen (YES) assay to compared toxicity of WW treated by AOPs such
404 as ultrasonication, Fenton's oxidation and ferro-sonication contaminated with carbamazepine.
405 Based on YES assay results, they reported that ultrasonication, Fenton's oxidation and ferro-
406 sonication pre-treated WW with carbamazepine is not estrogenic in nature. Chlortetracycline and

407 its metal complexes toxicity to Gram positive *Bacillus thuringiensis* (Bt) and Gram negative
408 *Enterobacter aerogenes* (Ea) bacteria in WWS was studied by Pulicharla et al. (2015). They
409 reported that CTC–metal complexes were more toxic than the CTC itself for Bt whereas for Ea,
410 CTC and its metal complexes showed similar toxicity and also concluded that CTC and its metal
411 complexes are toxic to bacteria when they are biologically available. Gaw and Glover (2016)
412 reported the contagious toxicity of isoprostanes present in WW to fish and aquatic invertebrates
413 through different activities such as reproductive impairment, oxidative stress and cardiovascular
414 disturbance. Isoprostanes are produced by free radical catalyzed peroxidation of essential
415 polyunsaturated fatty acids such as docosahexaenoic acid, arachidonic acid, and
416 eicosapentaenoic acid. They reported that isoprostanes as products and effectors of oxidative
417 stress and exposure to it in WW may produce oxidative stress toxicity cascade like a contagious
418 disease throughout the receiving environment. Marshall et al. (2017) used LuminoTox as a tool
419 to monitor toxicity of treated effluent contaminated by ECs. They reported that LuminoTox was
420 able to detect the ECs mix with WW when it was present at a concentration range between 6
421 $\mu\text{g/L}$ to 50 $\mu\text{g/L}$ and also suggested that this technology can be used as an effective tool for WW
422 monitoring with the intent of detecting residual ECs. Further, estrogenic burden of five parabens
423 in WWS collected across the United States was reported by Chen et al. (2017). They reported
424 insignificant estrogenicity of parabens in sewage water as compared to the value calculated for
425 natural estrogens reported in the literature to occur in sewage water.

426 Typically toxicity of ECs can be evaluated by bioassay method by exposing test organisms to
427 specific concentrations of this compound. These bioassays are then used to calculate the
428 predicted no-effect concentrations (PNEC) and the results are then compared to the measured
429 environmental concentrations (MEC). Further, risk characterization which is an estimation of the

430 incidence of the adverse effect generally involves a risk quotient calculated between the highest
431 MEC and the PNEC. Munoz et al. (2008) used life cycle impact assessment model to quantify
432 the potential environmental impacts on ecotoxicity and human toxicity of ECs present in WW.
433 They reported that according to the model, toxicity of both influent and effluent is mainly caused
434 by the presence of PPCPs and there is substantial impact in reduction in ecotoxicity and human
435 toxicity (between 42% and 85%) after treatment of WW. Further, Naidu et al. (2016) presented a
436 risk based methodology for better management of ECs in surface water and WW. They
437 recommended trade-off between risk-reduction and cost-effectiveness as an alternative remedial
438 solution for managing ECs in environment. Further, they suggested that various strategies such
439 as waste minimisation, appropriate waste disposal, improved management and usage of
440 chemicals, limitation in discharge of chemicals and improved WW treatment systems must be
441 implemented for better management of risk of ECs to environment.

442 Further, toxicity can also occur due to the transform of ECs due to different WW treatment
443 processes such as AOPs, hydrolysis processes, and microbial degradation processes. During the
444 process of treatment, there may be formation of more toxic by-products than the parent
445 compound, which make it more important to track and characterize the transformation products
446 during different treatment processes. Advanced oxidation processes are often complex and lead
447 to multiple reaction products in the medium during the treatment process as demonstrated by
448 some dehydrated products of tetracyclines and photodegradation products of the fluoroquinolone
449 antibiotic ofloxacin (Halling-Sorensen et al. 2002). Farre et al. (2008) reported a review on
450 toxicity of ECs and its transformation products in the aquatic environment. They suggested that
451 the formation of aggregates in water offers the opportunity for ECs to become associated with
452 the aggregates, leading to change in bioavailability of these contaminants and create more

453 toxicological concerns. Sang et al. (2014) evaluated the toxicity of artificial sweeteners
454 acesulfame and sucralose and their by-products during photolysis of WW and reported that acute
455 toxicity for the by-products of both sweeteners revealed that the phototoxicity of acesulfame
456 degradation products may impact aquatic ecosystems. The persistent antiepileptic drug
457 carbamazepine, prevalent anti-inflammatory drug diclofenac and clofibric acid, a metabolite of
458 lipid-lowering agents clofibrate, etofibrate and etofyllin clofibrate, were well detected in WW.
459 The frequent occurrence and potential toxicity of diclofenac towards several organisms such as
460 fish and mussels by chronic exposure lead to severe toxic effects. Further, Fatta-Kassinos et al.
461 (2011) reported that diclofenac is not completely removed from WWTP due to its poor
462 degradation and higher consumption rates. Toxicity of diclofenac and its transformation products
463 in aquatic as well as terrestrial environment was reviewed by Lonappan et al. (2016). They
464 reported that the available ecotoxicology data of diclofenac showed acute toxic effects to many
465 organisms, such as mussels. Further, they recommended more studies to assess the fate and
466 toxicological effects of diclofenac and its metabolites by considering the possible interaction of
467 diclofenac with other contaminants. Further, toxicity can also occur when ECs and their
468 transformation products react with disinfectants in WWTPs. Shen and Andrews (2011) reported
469 that ECs containing amine groups can serve as nitrosamine precursors during chloramine
470 disinfection. Further, they reported that among all the ECs, ranitidine showed strong potential to
471 form nitrosodimethylamine (NDMA), even at environmentally relevant concentrations.

472 Further, recently engineered nanoparticles (ENPs) considered as ECs has also triggered
473 concerns relating to their potential environmental health implications with respect to aquatic
474 organisms, including bacteria, invertebrates and fish (Kaya et al. 2015). The ENPs produced
475 from nanomaterials that used in our household and industrial commodities in day today life find

476 their way through waste disposal routes into the WWTPs and end up to aquatic environment. The
477 impact of ENPs in WW microorganisms was reviewed by Brar et al. (2010). They concluded that
478 the release of ENPs to WWTPs can impact the system in two ways such as: (i) when present in
479 trace levels ($\mu\text{g/l}$ and/or ng/l), prior to WW recharge/reuse applications, ENPs can be removed
480 based on toxicity study data, and (ii) when present in higher concentration (mg/l), presence of
481 ENPs can affect the treatment plant by various mechanisms, including inhibition of
482 microorganisms in secondary treatment process, increasing the turbidity, fouling of membranes
483 or affecting the efficiency of disinfection processes. Toxic effect of ENPs on WW
484 microorganisms was reported by Eduok et al. 2013. They reported that ENPs and their
485 transformation products interact with naturally occurring substances in WW which further hinder
486 microbial degradation processes with increased potential for accumulation and toxicity. Toxicity,
487 risks and regulations of ENPs to environmental microorganisms was reported by Hegde et al.
488 2016). They reported that interactions of ecological microorganisms at molecular level to ENPs
489 are limited by the cost-effective analytical methods and further suggested for a multidisciplinary
490 approach combining experimental, computational and theoretical approaches to understand and
491 tackle the ecotoxicological problems associated with these ECs. Goswami et al. (2017) reviewed
492 the nature, behavior and eco-toxicity of ENPs to environment. They reported that ENPs and their
493 transformed products can reduce cell viability, growth and morphology of living organisms
494 leading to enhanced oxidative stress, and DNA damage. The effect of TiO_2 nanoparticles on the
495 oxygen uptake rate in three different types of WW such as synthetic, raw, and filtered was
496 evaluated by Cervantes-Aviles et al. (2017). They observed an overarching pattern of cell
497 membrane disruption for all type of WW during the interaction between TiO_2 nanoparticles and
498 microorganisms. Further, persistent occurrence and fate of ECs in WW leads to development of

499 advanced analytical methods to determine the concentration of ECs prior to selection of the pre-
500 treatment or treatment method to eliminate the same.

501 **5. Advancement in analytical techniques for emerging contaminants analysis in wastewater**

502 One of the major limitations in the analysis of ECs in complex matrices such as WW remains
503 the lack of methods for quantification at low concentrations. The prerequisite for proper risk
504 assessment and monitoring of ECs in WW is the availability of multiresidual methods that permit
505 measurement at the low ng/L level (or even much lower concentrations). In the WWTPs, influent
506 and effluent are the matrices most often used for development of a reliable, fast and efficient
507 procedure for performing quantitative target analysis of ECs. Sample pre-treatments, such as
508 isolation of analytes, purification of extracts and pre-concentration, are required to avoid matrix
509 effects that exert a detrimental impact on important quantification parameters including limit of
510 detection (LOD), limit of quantification (LOQ), linearity, accuracy, and precision.

511 Occurrence of ECs in WW has been analyzed mainly by chromatographic methods. For
512 quantification of ECs in WW, Bizkarguenaga et al. (2012) used solid phase extraction (SPE)
513 combined with large volume injection-programmable temperature vaporization–gas
514 chromatography–mass spectrometry (LVI–PTV–GC–MS). For simultaneous extraction and the
515 multiresidue determination of ECs in WW samples, they optimized SPE variables such as the
516 nature of the solid phase (C18, Oasis-HLB, and Lichrolut), sample volume, addition of NaCl and
517 MeOH, pH of the water phase and the volume of the eluent solvent. They reported that the LODs
518 obtained for all the target compounds were at low ng/L level and the best results were obtained
519 after the clean-up of the sample using Florisil cartridges. Determination of nitrosamines and
520 caffeine metabolites in WW using GC-MS and suitability of ionic liquid (IL) such as SLB-IL59,
521 SLB-IL61, SLB-IL82 and SLB-IL111 as stationary phases for GC-MS was reported by Reyes-
522 Contreras et al. (2012). They reported that the SLB-IL111 column enabled the baseline

523 separation and quantification of 7 nitrosamines in a shorter analysis time compared with
524 cyanopropylphenyl polysiloxane commonly used and further, SLB-IL59 column provided the
525 best results for caffeine metabolites. Prebihalo et al. (2015) used two-dimensional gas-
526 chromatography coupled with time-of-flight mass spectrometry (GC × GC–TOFMS) for
527 analyzing ECs in WW. They reported that the analytical technique permitted the identification of
528 halogenated benzotriazoles in WW and further, the use of GC × GC–TOFMS technique proved
529 to be a valuable tool in resolving complex matrices, as it allows the analyst to separate target
530 compounds.

531 Sample pre-treatment by SPE and the subsequent determination by liquid chromatography-
532 tandem mass spectrometry (LC–MS/MS) is the preferred technique for the analysis of ECs in
533 WW. Nurmi and Pellinen (2011) used ultra performance liquid chromatograph–time-of-flight
534 mass spectrometer (UPLC–TOFMS) for analysis of ECs in WW. They reported that the use of
535 two SPE sorbent materials as the sample pre-treatment technique strengthens the extraction of
536 diverse compounds and further multi-residue screening method can be used to analyse a variety
537 of ECs in WW from ng/L to µg/L level. Further, Robles-Molina et al. (2014) used multi-residue
538 method for the determination of over 400 ECs in WW by solid-phase extraction and liquid
539 chromatography-time-of-flight mass spectrometry. They reported that the use of SPE with Oasis
540 HLB permitted reasonable recovery rates and the overall performance of LC–TOF-MS for
541 quantification was satisfactory for most of the target compounds. Further, multi-residue analysis
542 of 90 ECs in WW by ultra-high-performance liquid chromatography tandem mass spectrometry
543 with application of a novel buffer, ammonium fluoride improved signal response in negative
544 ionisation mode was carried out by Petrie et al. (2016). They reported that by using this
545 analytical methodology, sensitivity of steroid estrogens was improved by 4–5 times in

546 environmental extracts and further application of the method revealed several metabolites
547 increased in concentration during WW treatment demonstrating the possible higher toxicity of
548 by-products as compared to parent compound. Determination of macrolide antibiotics, their
549 synthesis intermediates and transformation products in WW by using LC–MS/MS was reported
550 by Senta et al. (2017). They reported that by using an additional extract clean-up on strong
551 anion-exchange cartridges (SAX) resulted in high recoveries and accuracies, low matrix effects
552 and improved chromatographic separation of the target macrolide antibiotics, their synthesis
553 intermediates and transformation products in WW.

554 For fast determination of ECs in WW, Campos-Mañas et al. (2017) used direct injection
555 coupled to ultra-high-performance liquid chromatography quadrupole-linear ion trap analyser -
556 tandem mass spectrometry (LC–QqLIT–MS/MS). They reported that use of direct injection
557 reduced sample handling and solvent consumption and further the developed optimised method
558 showed low LODs (1 to 357 ng/L), leading to identification of up to 67 ECs in real WW samples
559 at concentrations ranging from 10 ng/L to 26.7 mg/L. Further, Comtois-Marotte et al. (2017)
560 used high resolution mass spectrometry with a Q Exactive orbital ion trap for the detection and
561 quantification of 31 ECs in solid and water samples including WW. They reported that the use of
562 a SPE sorbent with different retention processes and multiple elution steps allowed to extract
563 large set of ECs presenting a wide range of physico-chemical properties. Further, they reported
564 higher recoveries of target compounds from WW by using the Q Exactive mass spectrometer in
565 both full scan and MS/MS modes and also the developed analytical method showed good
566 linearity, precision, and accuracy for many of the target ECs.

567 Ultrafast quantification of carbamazepine in WW by LDTD–APCI–MS/MS approach was
568 carried out by Mohapatra et al. (2012b). They reported that LDTD–APCI–MS/MS method is

569 suitable for the rapid detection and quantification of carbamazepine in WW and help to
570 overcome the traditional use of liquid chromatography which composes use of expensive organic
571 solvents, cost of maintenance of chromatography pumps and replacing chromatography columns.
572 Boisvert et al. (2012) developed a new LDTD–APCI–MS/MS based approach for detection and
573 quantification of pesticides and pharmaceuticals in WW samples. Further, to optimize recovery
574 efficiencies, they evaluated different SPE parameters such as loading flow rate, extraction pH,
575 volume of sample, nature of the stationary phase, and composition of the washing solution for
576 extracting target analytes from WW. They reported 78% to 106% recoveries of target compound,
577 30 to 122 ng/L limit of detection, 90 to 370 ng/L limit of quantification and intraday and interday
578 coefficient of variation below 15%, showing a good precision of the developed method. Further,
579 the chelation activity of chlortetracycline with metal ions and formation of different intermediate
580 products and their quantification in WW by using LDTD–MS/MS approach was studied by
581 Puicharla et al. (2014). They reported the development of a new rapid and sensitive method for
582 quantification of chlortetracycline in WW and validated the method by studying linearity,
583 recovery, precision and the method detection limit. Further, this study demonstrated that
584 chlortetracycline was present in WW samples in varying concentrations ranging from 8 to 61
585 µg/L. Lonappan et al. (2016) compared LDTD–APCI–MS/MS approach with an established LC–
586 ESI–MS/MS method for quantification of diclofenac in WW. They reported that the newly
587 developed LDTD-APCI-MS/MS method reduced the analysis time to 12 s compared to 12 min
588 for LC–ESI–MS/MS method and further suggested that LDTD–APCI–MS/MS method can be
589 effectively used for the detection and quantification of diclofenac in WW samples instead of
590 traditional slow, matrix sensitive LC–ESI–MS/MS method.

591 **6. Conclusions and future challenges**

592 Treating and reusing wastewater is one of many means to improve water supply capacity,
593 especially within developing countries. The presence of a class of persistent emerging
594 contaminants including; endocrine disruptor compounds and pharmaceutical and personal care
595 products, raise questions about the re-use and recycle of the wastewater. Advancement in
596 wastewater treatment processes such as advanced oxidation processes including ozonation,
597 ultrasonication, catalysis processes, photooxidation and Fenton's oxidation, which generate
598 hydroxyl radicals in medium, are promising methods for removal of ECs from wastewater.
599 However, more investigation is required particularly on the combined application of these
600 treatment methods with biological treatment to make advantage of synergistic effects, and further
601 more attention towards identification of reaction intermediates, development of rate expressions
602 based on established reaction mechanisms, identification of scale-up parameters and criteria for
603 cost effectiveness with simultaneous higher degradation of the target compound. Further, in-
604 depth studies and concurrent engineering that applies the multi-disciplinary knowledge
605 developed from such studies are required to advance and apply new and emerging removal
606 pathways of emerging contaminants at different wastewater treatment steps, for which limited
607 data is available in the literature.

608 To obtain better precision and sensitivity and to quantify emerging contaminants in trace
609 concentrations in complex matrices such as wastewater, several advanced analytical methods
610 such as LVI-PTV-GC-MS, GC \times GC-TOFMS, LC-ESI-MS/MS, LC-QqLIT-MS/MS and
611 LDTD-APCI-MS/MS have been developed and optimized. Furthermore, new ultrafast methods
612 have been developed in order to minimize the sample preparation time, analysis time, sample
613 pre-treatment and cost by eliminating column use and reducing solvent consumption. Further,
614 development of advanced analytical techniques for quantification of emerging contaminants in

615 wastewater must follow the toxicology studies with a variety of endpoints such as cytotoxicity,
616 endocrine disruption, antibiotic resistance, and genotoxicity that are relevant to potential human
617 health or ecological health effects.

618 **Acknowledgement**

619 Authors would like to acknowledge the technical discussion with Canadian industry partners
620 through the Environmental Advances in Mining Program at the National Research Council of
621 Canada in outlining this review.

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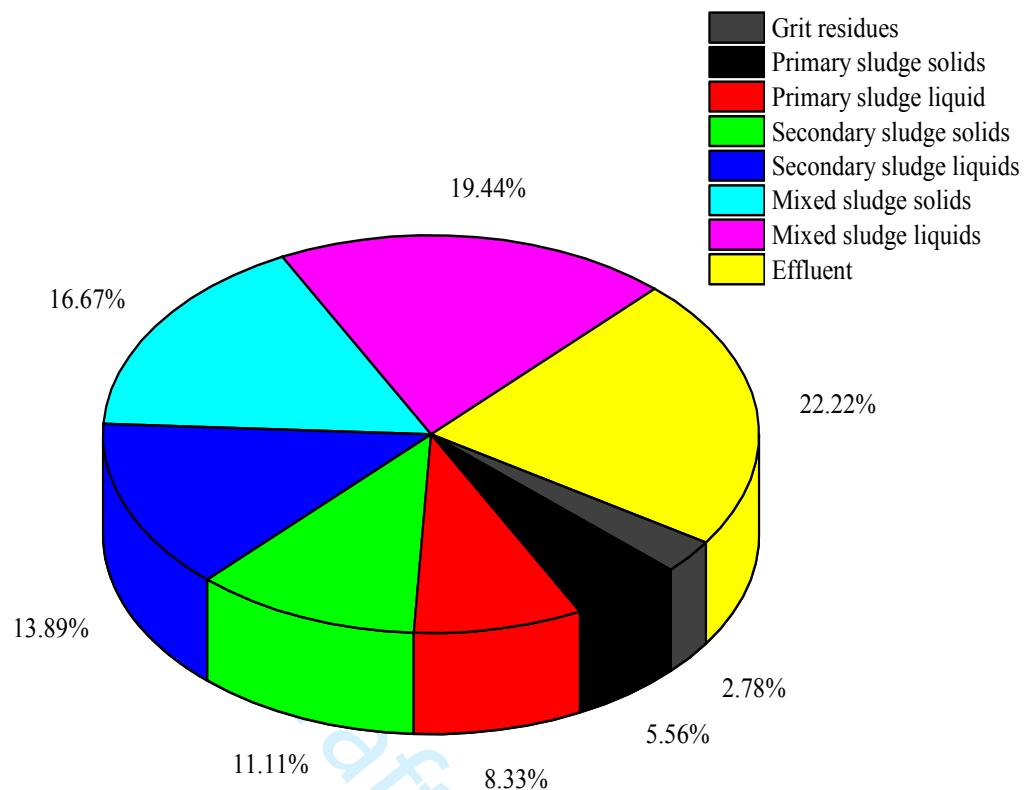


Fig. 1. Schematic presentation of distribution of ECs based on solid–water distribution coefficient (K_d) value in different compartments of wastewater treatment plant. Quantities of ECs are expressed relative to value observed in the influent (%). (data from Sun et al. 2017; Karthikraj and Kannan 2017; Tohidi and Cai 2017; Martinez-Alcala et al. 2017; Baalbaki et al. 2016; Fairbairn et al. 2016; Puicharla et al. 2014; Mohapatra et al. 2011).

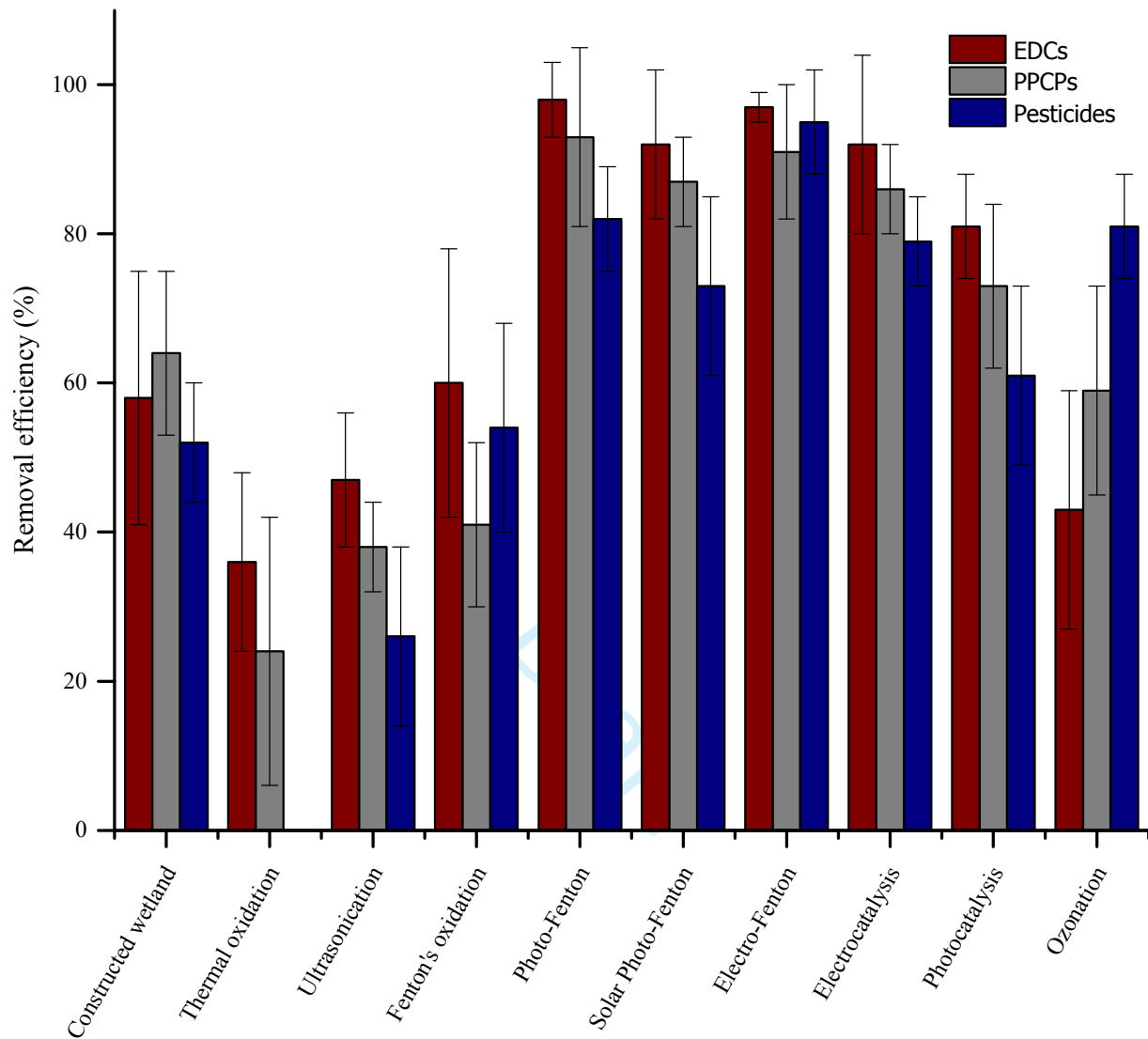


Fig.2. Average removal efficiency of emerging contaminants from wastewater during different advanced treatment processes. (data from: Matamoros et al. 2017; Pulicharla et al. 2017; Sun et al. 2017; Wang and Bai et al. 2017; Perez et al. 2017; Moreira et al. 2017; Zheng et al. 2016; Klancar et al. 2016; Avila et al. 2015; Guedes et al. 2015; Sharif et al. 2014; Daghrir et al. 2014; Mohapatra et al. 2014; Li et al. 2014; Mohapatra et al. 2013; Ibanez et al. 2013; Mohapatra et al. 2012; Mohapatra et al. 2011).

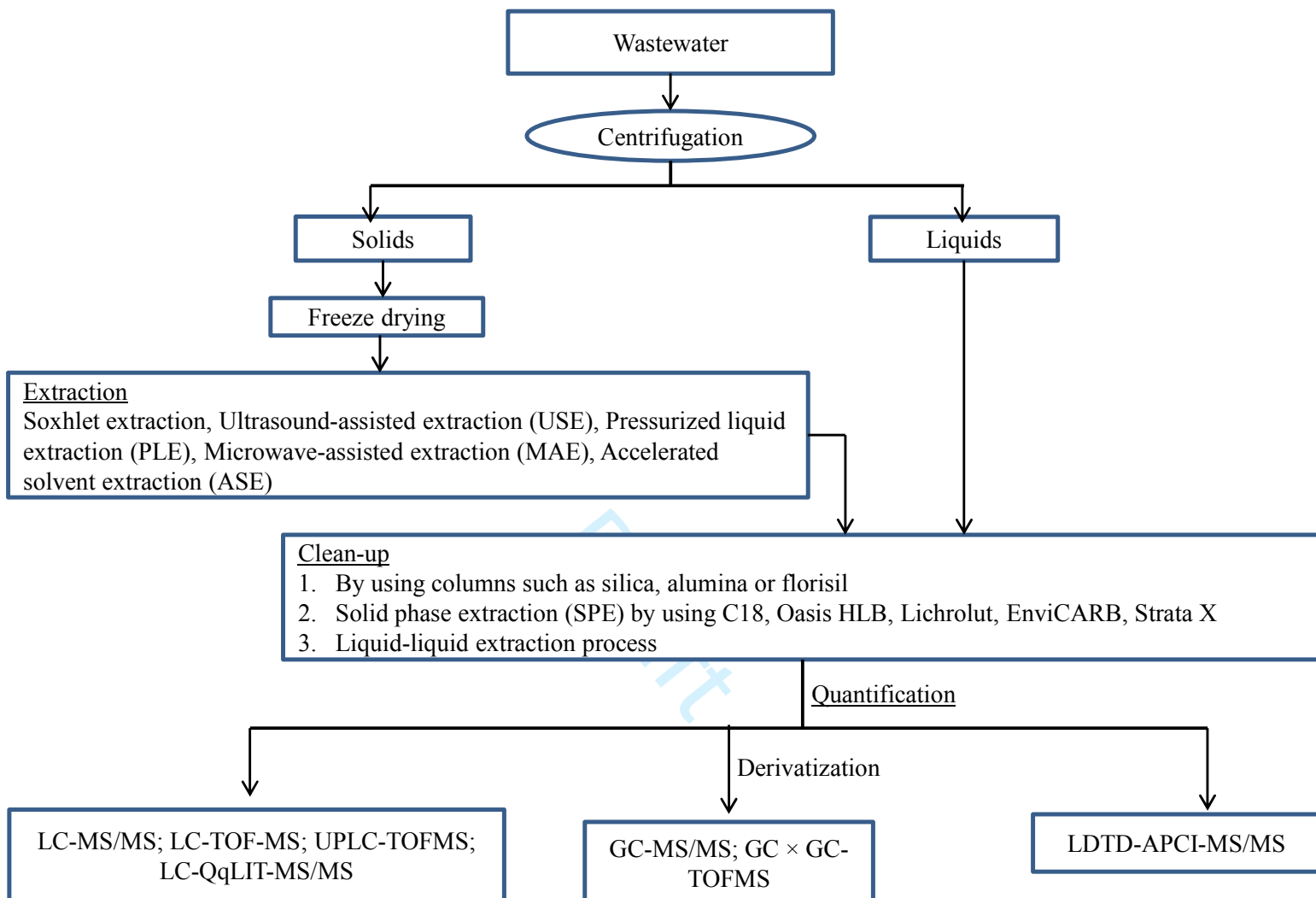


Fig.3. Analysis steps of emerging contaminants in wastewater by considering the fractionate approach in wastewater treatment plant

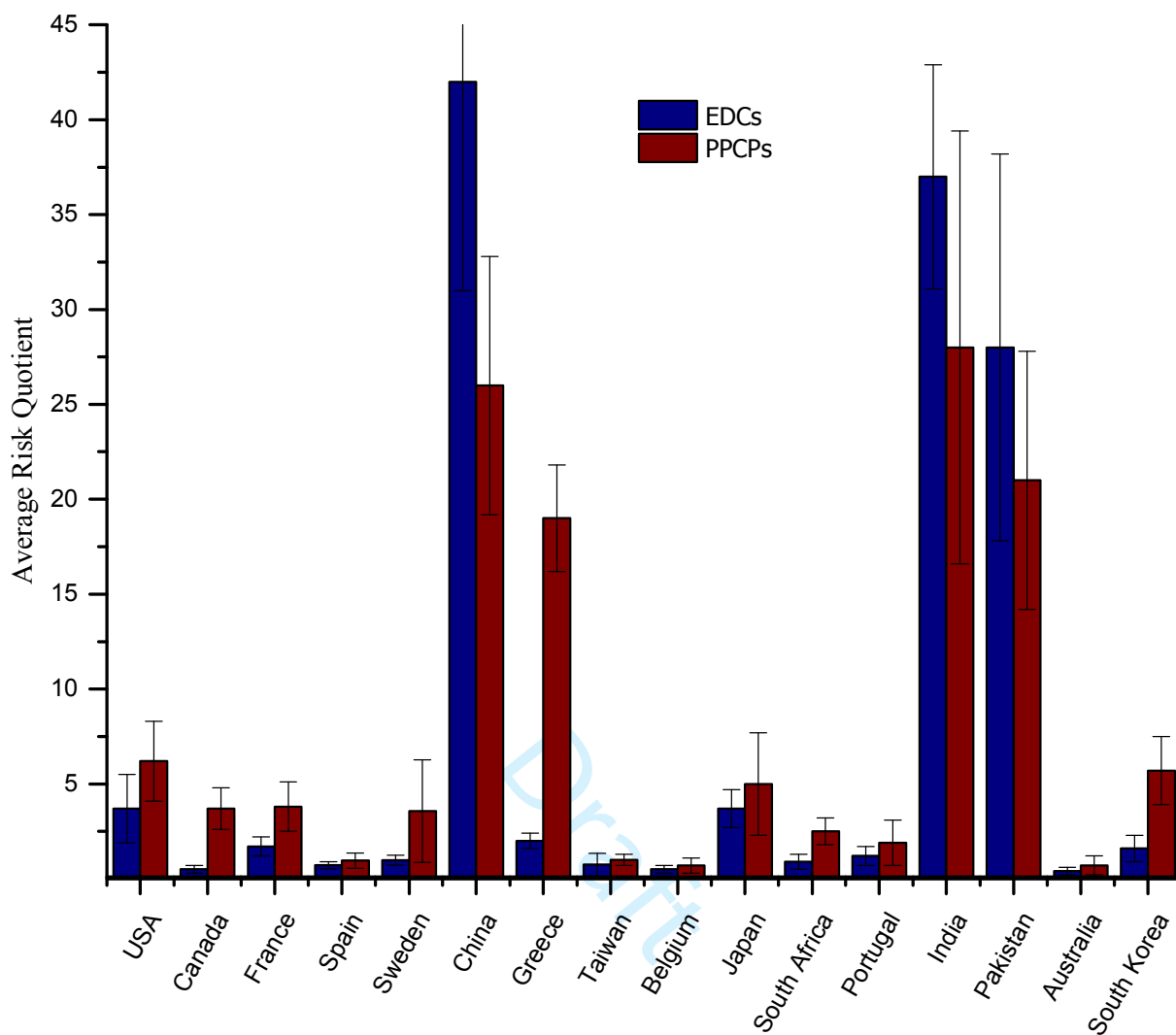


Fig.4. Country-wise average risk quotient (RQ) of emerging contaminants. $RQ > 1$ indicates an ecotoxicological risk for the aquatic environment due to the effluent load. $RQ < 1$ indicates no ecotoxicological risk for the aquatic environment due to the effluent load. Average value data from: USA (Hull et al. 2015, Blair et al. 2013, Kumar and Xagorarakis 2010); Canada (Hull et al. 2015, Carlson et al. 2013, Dussault et al. 2008); France (Minguez et al. 2016, Bouissou-Schurtz et al. 2014, Ferrari et al. 2003); Spain (Díaz-Garduño et al. 2017, González-Alonso et al. 2017, Afonso-Olivares et al. 2017, Molins-Delgado et al. 2016, Serra-Roig et al. 2016, Matamoros et al. 2015, Cristale et al. 2013); Sweden (Carlsson et al. 2006, Ferrari et al. 2003); China (Pintado-Herrera et al. 2017, Peng et al. 2017, Ding et al. 2017, Zhang et al. 2017, Wu et al. 2017, Liu et al. 2015, Yan et al. 2014, Wu et al. 2014); Greece (Thomaidi et al. 2017, Papageorgiou et al. 2016, Thomaidi et al. 2016, Thomaidi et al. 2015, Kosma et al. 2014, Stasinakis et al. 2012); Taiwan (Lin et al. 2015, Jiang et al. 2014); Belgium (Claessens et al. 2013); Japan (Guo and Iwata 2017); South Africa (Archer et al. 2017, Manickum and John 2014); Portugal (Pereira et al. 2017, Santos et al. 2017, Silva et al. 2014); India (Selvaraj et al. 2014, Singh et al. 2014, Malarvizhi et al. 2012, Ramaswamy et al. 2011); Pakistan (Ashfaq et al. 2017); Australia (Cao et al. 2010); South Korea (Kim et al. 2007).