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Chemical coagulation-based processes for trace organic contaminant removal: Current state and future potential

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2

3 **Abstract**

4 Trace organic contaminants have become an increasing cause of concern for governments

5 and water authorities as they attempt to respond to the potential challenges posed by climate

6 change by implementing sustainable water cycle management practices. The augmentation of

7 potable water supplies through indirect potable water reuse is one such method currently

8 being employed. Given the uncertainty surrounding the potential human health impacts of

9 prolonged ingestion of trace organic contaminant, it is vital that effective and sustainable

10 treatment methods are utilized. The purpose of this article is to provide a comprehensive

11 literature review of the performance of chemical coagulation process in removing trace

12 organic contaminant from water. This study evaluated the removal data collated from recent

13 research relating to various trace organic contaminant during the coagulation process. It was

14 observed that there is limited research data relating to the removal of trace organic

15 contaminant using coagulation. The findings of this study suggest that there is a gap in the

16 current research investigating the potential of new types of coagulants and exploring

17 coagulation-based hybrid processes to remove trace organic contaminant from water. The

18 data analyzed in this study regarding removal efficiency suggests that, even for the

19 significantly hydrophobic compounds, hydrophobicity is not the sole factor governing

20 removal of trace organic contaminant by coagulation. This has important implications in that

21 the usual practice of screening coagulants based on turbidity (suspended solid) removal

22 proves inadequate in case of trace organic contaminant removal.

25

33   sulphate; PPCPs, pharmaceutical and personal care products; RO, reverse osmosis; THM,

34   trihalomethane

35

36   **1. Introduction**

37   The term trace organic contaminant refers to contaminants present in water and wastewater at

38   very low concentrations. Types of trace organic contaminant include endocrine disrupting

39   compounds (EDCs), pharmaceutical and personal care products (PPCPs), and disinfection by-

40   products (DBPs). PPCPs and EDCs, for example, can enter the water supply as a result of

41   domestic and industrial usage. Certain trace organic contaminant have been shown to impose

42   adverse impacts on human, wildlife and aquatic ecosystems (Ottinger et al., 2002; Purdom et

43   al., 1994). **Table 1** lists toxicological effects of various trace organic contaminant on human

44   and aquatic organisms as reported in the literature.

45

46   Trace organic contaminant have become an increasing cause of concern for governments and

47   water authorities around the world as they attempt to implement sustainable water reuse

48   practices. The presence of PPCPs in potable water is of concern given that the impact of

49   prolonged low-level exposure on human health is not yet clearly understood (Daughton and

50   Ternes, 1999). In order to address the problem of water scarcity and the potential impacts of

51   climate change, indirect potable water reuse schemes are being implemented to augment the

52   water supply (Radcliffe, 2006). Therefore it is vital that effective water treatment processes

53   are employed to remove trace organic contaminant, and thus ensure that any potential human

54   health risks are mitigated prior to consumption. PPCPs as a category of trace organic

55   contaminant refer to a range of pharmaceutical and personal care products which can be

56   present in natural waterways and wastewater due to a variety of waste sources, including

57   household waste, hospital waste, and waste from pharmaceutical companies. PPCPs are

58 classified according to their compound class (e.g. antibiotic, stimulant, musk) which refers to

59 the intended purpose of the particular compound.

60

61 Chemical coagulation and flocculation in water/wastewater treatment involves the addition of

62 chemicals to alter the physical state of dissolved and suspended solids and facilitate their

63 removal by sedimentation (Duan and Gregory, 2003; Matilainen et al., 2010). Coagulants

64 react with the suspended and colloidal particles in the water, causing them to bind together

65 and thus allowing for their removal in the subsequent treatment processes (Lia et al., 2006).

66 The aggregation mechanisms through which particles and colloids are removed include a

67 combination of charge neutralization, entrapment, adsorption and complexation with

68 coagulant ions into insoluble masses (Duan and Gregory, 2003; Matilainen et al., 2010;

69 Verma et al., 2012).

70

71 Coagulation treatment forms an integral part of the conventional water treatment scheme.

72 Traditionally coagulation treatment has been employed in water treatment to decrease

73 turbidity and color and to remove pathogens (Hai et al., 2007; Matilainen et al., 2010; Verma

74 et al., 2012). The hydrophobic and high molar mass fractions of natural organic matter

75 (NOM) can be efficiently removed by coagulation (Matilainen et al., 2010).

76 Coagulation/flocculation/precipitation processes have been intensively used for decolorizing

77 wastewater (Hai et al., 2007; Verma et al., 2012). Chemical coagulation is often applied to

78 augment biological phosphorous removal in activated sludge processes (Nguyen et al., 2010).

79

80 Although coagulation, in combination with the other physicochemical water treatment

81 processes of flocculation and sedimentation, has long been known to be effective for bulk

82 natural organic matter removal from water, it has traditionally been found to be inefficient in

83 removing trace organic contaminants (Choi, 2006; Dempsey and O'Melia, 1984; Huerta-

84 Fontela et al., 2011; Kim et al., 2007b; Le-Minh et al., 2010; Snoeyink and Chen, 1985;

85 Ternes, 2002; Vieno, 2007). Advanced water treatment processes such as adsorption (Bundy,

86 2007; Choi, 2006; Ternes, 2002) and reverse osmosis/ nanofiltration processes have been

87 found to be more effective in the removal of trace organic contaminant from water (Al-Rifai

88 et al., 2011; Comerton et al., 2008; Nghiem et al., 2004; Nghiem et al., 2003).

89

90 **Table 2** summarizes the advantages and disdvantages of the available techniques for trace

91 organic contaminant removal from water/wastewater. All methods listed here have some

92 advantages as well as some drawbacks, and a universal standalone process applicable for

93 majority of the trace organic contaminant is yet to be developed. In general, the advanced

94 processes are more energy intensive and complex in operation than conventional treatment

95 processes. Because chemical coagulation and flocculation is a cost-competitive, common

96 method, it is logical to investigate ways to improve their performance of trace organic

97 contaminant removal.

98

99 It is important to note that although the coagulation process has been shown to achieve

100 insignificant removal of certain trace organic contaminant, the process of coagulation and the

101 types of coagulants currently being used have not been designed for the purpose of trace

102 organic contaminant removal. Therefore opportunities exist to optimize the coagulation

103 process by selecting the most appropriate coagulants and potentially redesigning the

104 coagulation process to maximize trace organic contaminant removal. If the coagulation

105 process can be optimized, it may be possible to devise efficient, hybrid treatment processes.

106 Several coagulation-based hybrid processes can be contemplated in this connection. For

107 instance: coupling of coagulation process with membrane bioreactors (MBRs). MBRs have

108 been shown to outperform conventional activated sludge (CAS) processes in terms of

109 producing better quality effluent when considering water quality parameters such as total

110 organic carbon and total nitrogen (Hai and Yamamoto, 2011; Leiknes, 2009; Visvanathan et

111 al., 2000), however the superiority of MBR in terms of trace organic contaminant removal is

112 yet to be demonstrated convincingly. Variation in removal of hydrophilic and persistent trace

113 organic contaminant by MBR treatment has been reported (Clara et al., 2005; Kimura et al.,

114 2005; Tadkaew et al., 2011). The sorption mechanism of coagulation, combined with the

115 biodegradation mechanism of MBR, may be beneficial in terms of helping to mitigate the

116 problems of membrane fouling (Hai and Yamamoto, 2011; Le-Clech et al., 2006) associated

117 with MBR, and improving the overall trace organic contaminant removal efficiency (Leiknes,

118 2009). This combination of coagulation and biological processes, for example, has been

119 found to be effective in the treatment of textile dyeing wastewater (Zaisheng et al., 2009),

120 while it has also been shown to be effective in removing certain trace organic contaminant

121 (Serrano et al., 2010). Furthermore, because coagulation process is usually used for

122 phosphate removal from wastewater (Yang et al., 2010), the phosphate removal and trace

123 organic contaminant removal can potentially be combined in one step (Zhou, 2011).

124

125 In order to achieve the goal of development of next generation coagulants, and also to assist

126 in the development of hybrid treatment processes, it is important to know the efficiency of

127 current coagulation processes and the efficacy of the particular coagulants currently being

128 utilized. The aim of this study, therefore, is to evaluate in depth the extent to which the

129 conventional coagulation treatment units are able to remove varieties of groups of trace

130   organic contaminant from water. An analysis of the data available in the literature will also be

131   conducted in an effort to determine the most suitable types of coagulants, coagulant dosage,

132   and associated parameters. It is expected that this study will assist efforts to develop high

133   performance coagulants and efficient hybrid water treatment processes combining

134   physicochemical and biological processes. This is particularly pertinent given the need to

135   augment potable water supplies with water recycling schemes as a result of an increasing

136   population and the potential adverse impacts of climate change. In-depth reviews on the

137   coagulation process mechanisms in general (Duan and Gregory, 2003) and on its application

138   in natural organic matter removal (Matilainen et al., 2010) or dye wastewater treatment (Hai

139   et al., 2007; Verma et al., 2012) are available in the literature. However, a comprehensive

140   literature review indicates that a critical review on the aspect of trace organic contaminant

141   removal by coagulation process is lacking, and the current article aims to fill in this important

142   gap.

143

144   **2. Removal of varieties of trace organic contaminants**

145

146   The efficiency of conventional water and wastewater treatment units in removing trace

147   organic contaminant has been studied in a number of different forms ranging from bench-

148   scale tests to operational water/wastewater treatment plants. The research conducted to date

149   using the conventional coagulants, which were not specifically designed to remove trace

150   organic contaminants, indicates that coagulation is an inefficient method of removing trace

151   organic contaminants (Huerta-Fontela et al., 2011; Kim et al., 2007b; Le-Minh et al., 2010;

152   Ternes, 2002; Vieno, 2007). The following is a comprehensive review of current research

153   relating to the removal of various groups of trace organic contaminants. **Table 3** compiles the

154   data related to removal of individual compounds sorted according to compound class, while

155   **Table 4** presents a succinct summary of the data presented in **Table 3** to highlight the

156   average removal according to compound class.

157

158   **2.1 Pharmaceuticals**

159   The removal efficiency of coagulation process in the removal of trace organic contaminant

160   varies significantly, with complete removal observed only for a small number of compounds.

161   For instance, one particular study showed that coagulation using aluminium sulphate

162    $(Al_2(SO_4)_3)$, in combination with flocculation and sand filtration, was able to completely

163   remove five out of the thirty-five trace organic contaminant (pharmaceuticals) detected in the

164   raw water at a drinking water treatment plant (Huerta-Fontela et al., 2011). The five

165   pharmaceuticals completely removed included chlordiazepoxide, zolpidem, bromazepam,

166   clopidogrel and doxazosin. This study also noted removal efficiencies of around 80% for

167   three other pharmaceutical compounds, namely warfarin, betaxolol and hydrochlorothiazide.

168   The effective removal of the above mentioned eight compounds, with the exception of

169   hydrochlorothiazide, may be the result of a removal phenomenon known as partitioning,

170   given their relative hydrophobicity (Huerta-Fontela et al., 2011). However, the remainder of

171   the trace organic contaminant tested in this study showed less than 50% removal during this

172   treatment phase, indicating that coagulation, flocculation, and sand filtration are largely

173   inefficient in removing those pharmaceuticals.

174

175   Certain antibiotics, which are a type of pharmaceutical compound, have been found to be

176   removed reasonably effectively by coagulation (Choi et al., 2008). Choi et al (2008) reported

177   that four of the seven tested tetracycline antibiotics showed removal efficiencies of between

178   55% and 66%, from river water samples using polyaluminium chloride (PACl) coagulants.

179   The effective removal of the tested tetracycline antibiotics in this case may be due to the

180   effects of sweep coagulation in the river water samples, and charge neutralization in the

181   synthetic water samples, respectively (Choi et al., 2008). The most poorly removed antibiotic

182   seems to be sulfamethoxazole which has shown negligible removal using both ferric chloride

183   (Stackelberg et al., 2007; Suarez et al., 2009) and ferric sulphate (Westerhoff et al., 2005).

184

185   Stimulants and psychoactive drugs are types of pharmaceuticals which include prescription

186   medicines and illicit drugs, which may be used recreationally or abusively. The exact impact

187   on human health as a result of ingestion of stimulants through water remains unclear (Huerta-

188   Fontela, 2008). A particular study explored the removal of certain stimulatory drugs of abuse

189   using chlorination, coagulation, flocculation, and sand filtration (Huerta-Fontela, 2008). The

190   removal of the stimulants included in this study was generally poor with the exception of

191   amphetamine which was completely removed during the conventional treatment processes

192   (Huerta-Fontela, 2008). However, it should be noted that the direct contribution of

193   coagulation to the overall removal of these compounds is uncertain as the removal data was

194   only supplied for the entire conventional treatment phase.

195

196   **2.2 Musk fragrances**

197   Musk fragrances are personal care products which can be found in products such as

198   detergents and cosmetics. Some selected musks were shown to be removed to a high degree

199   when using coagulation and flocculation at an urban sewage treatment plant (Carballa et al.,

200   2005), and as a pre-treatment method for hospital wastewater (Suarez et al., 2009). The musk

201   compounds tonalide, galaxolide, and celestolide were removed from hospital wastewater by

202 83%, 79%, and 78%, respectively during coagulation and flocculation, with the high degree

203 of removal possibly attributed to the hydrophobic nature of these compounds (Suarez et al.,

204 2009).

205

206 **2.3 Steroids/hormones**

207 Estrogenic compounds are another form of trace organic contaminant which have been found

208 to be poorly removed using conventional water treatment units (Bodzek and Dudziak, 2006;

209 Bundy, 2007; Le-Minh et al., 2010). Estrogens are female sex hormones which can be found

210 in waterways as a result of human and animal waste. The impact of these trace organic

211 contaminant on aquatic ecosystems and human health have become a growing cause of

212 concern given the increased presence of estrogens in water as a result of the disposal of

213 expired medications from hospitals, pharmaceuticals, and households (Bodzek and Dudziak,

214 2006). Bodzek and Dudziak (2006) studied the potential of a hybrid treatment process

215 combining coagulation and nanofiltration in removing natural and steroidal sex hormones.

216 Polyaluminium chloride (PAX-18) was found to be the most suitable coagulant for this

217 purpose, with removal efficiency of greater than 30% observed for estriol, diethylstilbestrol,

218 and mestranol (Bodzek and Dudziak, 2006). Ferric sulphate as a coagulant however was

219 shown to be less efficient in removing the estrogens used in this study, with the exception of

220 estradiol where it produced similar removal to the polyaluminium chloride coagulant used

221 (Bodzek and Dudziak, 2006), while aluminium sulphate has shown negligible removal of

222 estrone (Le-Minh et al., 2010) and estradiol (Bundy, 2007; Le-Minh et al., 2010).

223

224 **2.4 Other EDCs**

225   Endocrine disrupting compounds (EDCs) refer to chemicals or compounds that interfere with

226   the endocrine system of a human or animal. The EDCs, other than hormones, observed in the

227   literature relating to coagulation as a removal method were phthalate plasticizers, herbicides,

228   insecticides, pesticides, and polycyclic aromatic hydrocarbons (PAHs). The phthalate

229   plasticizer compounds di (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), and

230   diethyl phthalate (DEP) displayed the best removal efficiencies using coagulation and

231   flocculation as part of a pilot-scale drinking water treatment plant, with 53%, 49%, and 46%

232   removal, respectively (Choi, 2006). This may be explained by the removal of natural organic

233   matter (NOM) onto which the phthalate plasticizer compounds with high octanol/water

234   partition coefficients or hydrophobicity remained adsorbed (Choi, 2006). Insecticides have

235   also been shown to be removed with varying degrees of success, with the compounds aldrin,

236   heptachlor (Le-Minh et al., 2010), and diazinon (Stackelberg et al., 2007), removed by 49%,

237   46%, and 33%, respectively. The remaining EDCs showed low removal efficiencies ranging

238   between 24-33%, and consisted of a pesticide, herbicide, and two polycyclic aromatic

239   hydrocarbons (PAHs) (Le-Minh et al., 2010; Stackelberg et al., 2007).

240

241   **2.5 Summary of compound group-specific removal performance**

242   It is interesting to note from **Table 3** and **4** that the musk fragrances investigated in various

243   studies consistently showed significant removal by coagulation. Good removal (near 50%)

244   was also obtained for pthalate plasticizers, but the amount of available data is not sufficient to

245   draw a meaningful conclusion. Pharmaceuticals of different compound classes on an average

246   received a removal of around 30%. However, given the great variations in physico-chemical

247   properties of the pharmaceuticals, the removal of compounds even within the same

248   therapeutic class was observed to vary significantly. For instance, out of the anti-

249 inflammatory drugs listed in **Table 3**, only diclofenac consistently showed around 70%

250 removal, which is significantly high compared to the average of 35(±23)% estimated for this

251 compound class (**Table 4**). The average removal of the compound class "stimulants" was

252 34(±34) % which may be attributed to the fact that the compounds within this class were

253 often poles apart in terms of their removal by coagulation—for instance, while complete

254 removal of amphetamine was observed, caffeine was barely removed (**Table 4**). It should be

255 also noted that significant variation in removal of the same compound (e.g., caffeine) may be

256 observed in different studies (Bundy, 2007; Huerta-Fontela, 2008; Westerhoff et al., 2005). It

257 has been suggested that the classification of trace organic contaminant according to their

258 intended use or origin can only be used to qualitatively predict the removal efficiencies of

259 compounds of similar molecular structure, having similar molecular features or

260 physicochemical properties (Hai et al., 2011; Tadkaew et al., 2011). Because certain

261 molecular features and physicochemical properties of the trace organic contaminants as well

262 as the operating parameters can govern their rate of removal during coagulation process

263 (Lefebvre et al., 2010), Section 3 will analyze the data presented in **Table 3** and **4** from the

264 point of view of the factors governing the performance of coagulation process.

265

266 **3. Factors governing removal efficiency**

267 **3.1 Coagulation process parameters**

268 The effectiveness of a coagulation unit may depend on several factors including coagulant

269 type and dosage, mixing conditions, pH, alkalinity, temperature as well as the presence of

270 divalent cations and concentrations of destabilizing anions (biocarbonate, chloride, sulphate

271 etc.)(Duan and Gregory, 2003; Matilainen et al., 2010; Verma et al., 2012). In view of the

272 availability of data, we will focus on the effect of type and dosage of coagulant and effect of

273 pH, alkalinity and temperature of water.

274

275 *3.1.1 Effect of coagulant type and dosage*

276 The effect of coagulant type and dosage on trace organic contaminant removal has been

277 reported in a few studies. The use of aluminium sulphate as a coagulant was proven to be

278 highly effective in removing certain hydrophobic pharmaceutical compounds, namely

279 chlordiazepoxide, zolpidem, bromazepam, clopidogrel, doxazosin, warfarin, and betaxolol

280 (Huerta-Fontela et al., 2011), however the coagulant dose used in obtaining these results was

281 not provided. Aluminium sulphate displayed poor removal efficiency (<5%) for both estrone

282 and estradiol using a dosage of 78 mg/L (Bundy, 2007; Le-Minh et al., 2010). However it has

283 been found to be reasonably effective in removing certain EDCs such as phthalate plasticizers

284 at a dosage of 50 mg/L (Choi, 2006).

285

286 Ferric chloride was particularly effective in removing three musk compounds, namely

287 tonalide, galaxolide, and celestolide, from hospital wastewater at a dosage of 25 mg/L

288 (Suarez et al., 2009). The removal of these compounds does not seem to be improved by

289 greatly increased dosages of ferric chloride, as another study has shown that 250 mg/L

290 applied to an urban sewage treatment plant yielded similar removal efficiencies (Carballa et

291 al., 2005). On the other hand, the removal of bisphenol A increased from 5% to 20% due to

292   doubling the ferric chloride dose (Carballa et al., 2005). Because acidic compounds remain

293   (partially) ionized in aqueous phase, comparatively higher coagulant dosage may be required

294   for their removal. For instance, Zorita et al. (2009) achieved less than 25% removal of

295   diclofenac by applying a ferric chloride dose of 70 mg/L as a tertiary treatment of sewage

296   wastewater, while in another study Carballa et al. (2005) reported 70% removal applying a

297   higher dose of 250 mg/L. Chang et al. (2004) reported negligible interactions between trace

298   estrone, and iron oxyhydroxide particulates formed on addition of hydrolyzable ferric salts.

299   An estrone concentration of 15 ng/L was used in this study. This scenario is quite different to

300   that obtained with a significantly higher estrone concentration ($\sim$0.1 g/L) where a strong

301   interaction between estrone and clay particles was observed (Lai et al., 2000), suggesting that

302   organics in trace concentration are particularly difficult to remove by coagulation.

303

304   Verma et al. (2012) reported that pre-hydrolyzed coagulants such as polyaluminium chloride

305   (PACl), polyaluminium ferric chloride (PAFCl), polyferrous sulphate (PFS) and polyferric

306   chloride (PFCl) may achieve better removal of soluble dyes as compared to the hydrolyzing

307   metal salts. A few similar examples of certain coagulants outperforming others in terms of

308   trace organic contaminant removal can be found in the literature. For instance,

309   polyaluminium chloride (PACl) was shown to outperform ferric sulphate in the removal of

310   certain estrogen compounds using dosages of 5.4 mg/L and 12.2 mg/L, respectively, however

311   removal efficiencies were not found to be greater than 40% for any of the estrogens tested

312   (Bodzek and Dudziak, 2006). In another study, Carballa et al. (2003) observed that PACl

313   achieved the highest removal of the studied musk fragrance compounds, while in the case of

314   diazepam, ferric chloride displayed the best removal. Choi et al. (2008) also utilized PACl,

315   with the best removal efficiencies in this study observed at a dosage of 40 mg/L, with

316 reported removal efficiencies of above 50% for four of the seven antibiotics tested. While

317 using PACl in dosages of above 2 mol/L, Wang et al. (2007) interestingly noted the absence

318 of Al_{13} ($AlO_4Al_{12}(OH)_{24}^{7+}$) species, which is reported to enhance NOM removal, whereas the

319 Al_{13} species were observed when a different coagulant (nano-Al_{13}) was used with the same

320 level of dosage. The superiority of PAFCl over PFS and PACl for decoloration of

321 petrochemical wastewater was demonstrated by Chen et al. (2010). They attributed the

322 superior performance of PAFCl to the fact that PAFCl combines the coagulatory advantages

323 of both aluminium and iron salts and is, hence, able to form more bulky flocs rapidly, leading

324 to rapid sedimentation. Similarly, inorganic salts in combination with organic polyelctrolytes

325 as coagulant aids or composite inorganic-organic coagulants (Matilainen et al., 2010) have

326 been reported to be beneficial in some instances. However, systematic studies on comparison

327 between the trace organic contaminant removal performance of various pre-hydrolyzed and

328 hydrolyzable coagulants could not be identified in the literature. A lack of studies on the

329 application of natural coagulants (e.g., polysaccharides, chitosan, guar gum etc.) (Verma et

330 al., 2012) for trace organic contaminant removal is also evident. Based on turbidity removal,

331 Zhou (2011) screened two cationic flocculants, one anionic flocculant and one coagulant

332 from a list of 20 different polymers. However, the finally selected coagulants achieved

333 negligible removal of the selected trace organic contaminant, indicating the limitation of

334 using turbidity removal as a criterion for selecting/designing coagulants for trace organic

335 contaminant removal.

336 It is worth-noting here that in addition to the type and dosage of coagulants that of the

337 flocculants can be important in determining the removal efficiency of trace organic

338 contaminants. However, in the literature the flocculation process has been was almost always

339 discussed as part of a combined process with coagulation (e.g. mentioned as

340   coagulation/flocculation), and specific details regarding the flocculation process such as

341   dosage and types of flocculants used have been rarely provided. As a result, it was not

342   possible to draw a meaningful conclusion relating to the impact of flocculant type and dosage

343   on the removal of trace organic contaminants.

344

345   *3.1.2 Effect of pH, alkalinity and temperature*

346

347   Changes in coagulants species and/or charge of the target compound can result due to

348   variation in pH of the liquid media (Yan et al., 2007; Yan et al., 2008; Zhao et al., 2008). In

349   addition to governing the coagulant speciation, the media pH influences the extent of

350   dissociation of the trace organic contaminants, and can, thereby, result in compound-specific

351   removal performance during application of a certain type of coagulant. A simultaneous effect

352   of coagulant species and the charge of the target compound can, therefore, be perceived.

353   Zhao et al. (2008) explained this phenomenon with the example of the removal of

354   trihalomethane (THM) and haloacetic acid (HAA) precursors with PACl. HAA precursors are

355   mainly aromatic while the THM precursors contain more aliphatic moieties. At pH 5.5, the

356   negatively-charged aliphatic THM precursors may be removed due to charge neutralization

357   by the monomeric Al species that exists under that pH. However, because both the Al_{13} and

358     $Al(OH)_3$ species exist at a higher pH (5.5—7.5), both charge neutralization precipitation and

359   adsorption could be responsible for THM removal in that case. On the other hand, in the case

360   of HAA precursors, self-aggregations of the aromatic and hydrophobic functional groups can

361   occur under acidic pH, while adsorption onto flocs and subsequent removal through sweep

362   flocculation may occur under alkaline pH. However, certain compounds may show negligible

363   removal by coagulation over a wide range of pH. For instance, although Chang et al. (2004)

364 observed a significant effect of pH on total organic carbon removal, no obvious change in

365 estrone removal was observed for coagulation under different pH conditions (5—11.4).

366

367 Some coagulants, upon application, can cause pH change of water. The natural pH of ferric

368 chloride, ferric sulphate as well as alum solution is acidic. Hence, certain basic compounds

369 (e.g., lime or sodium hydroxide) need to be added to adjust the pH to neutral. This may lead

370 to production of extra sludge. However, Westerhoff et al. (2005) reported that the application

371 of a ferric sulphate coagulant at a low pH may be quite effective in removing ionic

372 pharmaceuticals from water with a high amount of humic material. Vieno et al (2006),

373 however, achieved moderate removal of the pharmaceutical compounds ibuprofen, diclofenac

374 and bezafibrate by employing a ferric sulphate coagulant at a pH of 4.5. PACl coagulants are

375 pre-neutralized, have smaller effect on the pH of water and therefore reduce the need of such

376 pH correction. However, a higher dose of a coagulant may be required unless the natural pH

377 of water is adjusted to a level suitable for the coagulant. Yan et al. (2008) noted that a higher

378 dose of PACl was required for treating a highly alkaline river water. Optimum sweep

379 coagulation refers to the point where significant interaction occurs between the colloidal

380 particles and the precipitated polymeric hydroxides (Vieno et al., 2006). Choi et al. (2008)

381 found that optimum sweep coagulation occurred in river water at a pH of 7.4 and PACl

382 dosage of 60 mg/L, and at a pH of 6.8-8.3 and aluminium sulphate dosage of 20-50 mg/L.

383

384 The detrimental effect of lower temperature (for instance, 1°C as compared to 25 °C) over

385 turbidity or color removal efficiency of coagulants is well known (Duan and Gregory, 2003;

386 Matilainen et al., 2010; Verma et al., 2012). However, only a handful of studies have

387 specifically studied the effect of temperature in case of trace organic contaminant removal by

388   coagulation process. By conducting investigations under two different temperatures (12° and

389   25° C), Carballa et al. (2003) reported negligible difference in removal of galaxolide, tonalide

390   and diclofenac.

391

392   **3.2 Effect of physico-chemical properties of trace organic contaminants**

393   Various physico-chemical properties of the target trace organic contaminant may exert

394   profound effects on the efficiency of the coagulation process. Differences have been noted

395   between the removal of acidic and neutral trace organic contaminant, with the latter showing

396   higher removal efficiencies in a study on the removal of PPCPs from municipal wastewater

397   using coagulation and flocculation (Carballa et al., 2003). Lipophilic compounds, like musks,

398   are mainly absorbed on the lipid fractions of the sludge, while acidic compounds, like

399   diclofenac, are mainly adsorbed due to electrostatic interactions (Carballa et al., 2005). The

400   partition coefficient, Log D, is a physicochemical parameter that measures the

401   hydrophobicity of a compound at a given pH. It has been suggested that the sorption of trace

402   organic contaminants to activated sludge is related to the hydrophobicity of a compound, and

403   thus the Log D value of a compound at a given pH (Wells, 2006). A study using a laboratory

404   scale MBR system found that significantly hydrophobic (Log D > 3.2) trace organic

405   compounds were removed with a high degree of efficiency (Tadkaew et al., 2011). The

406   relationship between hydrophobicity and removal efficiency has also been shown in the case

407   of the coagulation process. For instance, a study relating to the removal of pesticides from

408   surface water using coagulation and flocculation found that the main mechanism governing

409   the removal of these trace organic contaminant was sorption onto the natural material in the

410   river water (Thuy et al., 2008). Trace organic contaminant can also partition into the

411   hydrophobic domain in colloidal organic matter. Rebhun (1998) utilized dissolved humic acid

412   (DHA) to remove hydrophobic contaminants (polycyclic aromatic hydrocarbons, PAHs) from

413   water by complexation−flocculation process. Dissolved humic acid was added to the

414   contaminated water and allowed to interact (bind) with the dissolved contaminants to form

415   DHA−contaminant complexes (complexation stage). A flocculant was then added, resulting

416   in precipitation and flocculation of the DHA and the associated contaminant. Similarly,

417   hydrophobic partitioning has been noted as a potential reason for the effective removal of

418   certain pharmaceutical compounds (Huerta-Fontela et al., 2011), and certain musk

419   compounds (Suarez et al., 2009). This is consistent with another study exploring the removal

420   of EDCs and PPCPs by coagulation, where it was found that neutral compounds with higher

421   hydrophobicity displayed better removal efficiencies (Westerhoff et al., 2005). These

422   findings relating to the removal of these neutral, hydrophobic musk compounds are consistent

423   with another study where a ferric chloride coagulant was directly added into   conventional

424   activated sludge (CAS) reactors (Serrano et al., 2010).

425

426   Reports in contrary to the above examples demonstrating a correlation between

427   hydrophobicity (Log D) and/or charge of a compound and its removal by coagulation process

428   do, however, exist. A poor correlation between Log D and adsorption was found when

429   hydrophobic partitioning was less relevant, i.e., when the solutes were small, hydrophilic

430   and/or charged/polar (de Ridder et al., 2010). However, Carballa et al. (2003) noted

431   differences in removal efficiencies even between neutral compounds. They observed that

432   while the tested musk fragrances (galaxolide and tonalide) showed removal efficiencies

433   between 50-70%, certain pharmaceuticals (diazepam and carbamazepine) showed very low

434   removal despite being neutral compounds. The neutral pharmaceutical compounds diazepam

435   and carbamazepine have been consistently shown to be poorly removed. Coagulation has

436 been found to have no impact on the removal of diazepam (Huerta-Fontela et al., 2011;

437 Suarez et al., 2009), and very little impact on the removal of carbamazepine (Suarez et al.,

438 2009; Ternes, 2002; Vieno et al., 2006; Vieno, 2007). On the other hand,

439 hydrochlorothiazide, despite having relatively smaller Log D than carbamazepine and

440 diazepam, has been reported to be significantly removed by coagulation using alum (Huerta-

441 Fontela et al., 2011). In contrast, hormones (estrogens and progesterone), which possess

442 significantly high Log D (Tadkaew et al., 2011) have been consistently shown to be poorly

443 removed by coagulation treatment (**Table 3**).

444

445 **Figure 1** plots the Log D values (at a pH of 7) of trace organic contaminant listed in **Table 3**

446 against their removal efficiency data. The information displayed in **Figure 1** suggests that

447 there is no discernable link between hydrophobicity (Log D) and removal efficiency for the

448 compounds in these studies. The most common pH values utilized for the coagulation phase

449 of the studies reviewed in this paper were around 5 and 7. Accordingly, the graph was re-

450 plotted (not shown) with Log D values at a pH of 5; however, a similar trend was observed.

451 Therefore, based on the literature reviewed here, hydrophobicity appears not to be the sole

452 factor governing the removal of trace organic contaminant using coagulation, even when the

453 compound is significantly hydrophobic (Log D > 3.2). To remove the target trace organic

454 contaminants from a particular wastewater, coagulants are commonly selected according to

455 turbidity (suspended solids) removal from that wastewater, since it is usually expected that

456 hydrophobic organics may partition onto settled solid particles and be removed (Zhou, 2011).

457 However, the observation made through **Figure 1** suggests that coagulant selection based on

458 only turbidity (suspended solids) removal may not be always effective. Information on no

459 alternative suitable indicator could be found in the literature.

460

461   The extent of adsorption can be related to the structures of the target compounds. Yu et al.

462   (2002) reported on the effect of dye structure on the interaction between a selected set of

463   organic flocculant and dye. They observed that the process of dye flocculation is controlled

464   by both charge and hydrophobic interactions. However, there has rarely been any specific

465   study with the coagulant—trace organic contaminant combination from this aspect.

466   Haberhauer et al. (2000) reported increased adsorption due to replacement of the methyl

467   group of the phenoxy ring of a phenoxyalkanoic herbicide by a chlorine (dichlorprop) and

468   additional increase due to the substitution of the propionic moiety by an acetic acid moiety

469   (2,4-D). They attributed this to the effect of such structural change on the volume and

470   polarity of the investigated compounds.

471

472   **4. Coagulation-based combined/hybrid processes**

473

474   Use of advanced water treatment processes in conjunction with coagulation process have

475   often been found to improve the overall removal efficiency of trace organic contaminant in

476   both laboratory investigations and operational drinking water treatment plants (Bundy, 2007;

477   Choi, 2006; Huerta-Fontela, 2008; Lefebvre et al., 2010; Ternes, 2002). A few such examples

478   are given below.

479

480   **4.1 Combination with activated carbon adsorption**

481   A properly designed coagulation-flocculation unit can efficiently remove suspended solids

482   and can thereby enhance the performance of a subsequent activated carbon adsorption unit by

483   reducing competitive adsorption (Hai et al., 2007). For instance, in the case of dye effluent

484 treatment, coagulation followed by adsorption was reported to produce effluent of reuse

485 standard, while reducing the coagulant consumption by 50%, hence lowering the volume of

486 sludge formed, in comparison to coagulation only (Papic et al., 2004). Treatment methods

487 employing coagulation and flocculation followed by filtration with granular activated carbon

488 (GAC) have been reported to be very effective in removing certain trace organic contaminant

489 during drinking water treatment (Bundy, 2007; Choi, 2006; Ternes, 2002). GAC post-

490 treatment has been found to significantly enhance the removal efficiency to almost complete

491 removal of caffeine, trivoflaxin mesylate and estradiol (Bundy, 2007), carbamazepine,

492 bezafibrate and diclofenac (Ternes, 2002), cocaine, 3,4-Methylene dioxy methamphetamine

493 (MDMA) and benzoylecgonine (Huerta-Fontela, 2008). GAC following coagulation has also

494 been reported to be reasonably effective in removing certain tetracycline antibiotics (Choi et

495 al., 2008). Tomaszewska et al. (2004) investigated the removal efficiency of humic acid and

496 phenol by coagulation and adsorption (powdered activated carbon, PAC) and revealed that in

497 comparison to coagulation alone, the integrated adsorption-coagulation system is effective in

498 removing phenol. Zhang et al. (2011) reported an enhanced phenol removal in a process

499 involving combined application of the common coagulant aluminum chloride and manganese

500 dioxide formed in situ. Nanotechnology has appeared as a very promising new way to

501 remove organics from water (Matilainen et al., 2010).Nanomaterials have exceptional

502 adsorption properties and they are able to entrap diverse organic molecules, including those

503 in trace concentrations (Joseph et al., 2011; Upadhyayula et al., 2009). Analysis of the mode

504 of action of such adsorbents may be beneficial while carrying out fundamental research on

505 development of high performance coagulants.

506

507 **4.2 Combination with nanofiltration/ reverse osmosis**

508 Combination of coagulation, flocculation, and membrane filtration has been described as an

509 efficient and reliable treatment option for surface waters with high NOM concentrations

510 (Leiknes, 2009). The use of coagulation prior to nanofiltration (NF) may help to streamline

511 the transport properties of NF by removing almost all of the NOM in the water (Bodzek and

512 Dudziak, 2006) so that trace organic contaminants can be efficiently removed by NF. Muller

513 and Uhi (2009) reported that a single-tank coagulation—ultrafiltration process removed high

514 molecular weight organics (preferentially humics) from raw water and subsequently

515 improved the adsorption of the trace compound cis-1,2-dichloroetheneon onto granular

516 activated carbon.

517

518 **4.3 Combination with advanced oxidation processes (AOPs)**

519 Because high concentrations of suspended or colloidal solids in the wastewater may impede

520 the advanced oxidation processes, sufficient prior removal of these materials by a

521 physicochemical treatment such as coagulation is required (Ciardelli and Ranieri, 2001; Hai

522 et al., 2007). Ozonation, when employed as a treatment process following conventional water

523 treatment, has been reported to be very effective in removing trace organic contaminant

524 (Huerta-Fontela, 2008; Ternes, 2002). Similarly to GAC, ozonation has been shown to

525 effectively remove carbamazepine, bezafibrate, diclofenac (Ternes, 2002), and caffeine

526 (Huerta-Fontela, 2008). A hybrid coagulation-membrane reactor may be placed subsequent to

527 an advanced oxidation process in order to remove soluble degradation products (Hai et al.,

528 2007). Chemical coagulation following Fenton treatment has been found to reduce floc

529 settling time, enhance decoloration, and reduce soluble iron in effluent (Hai et al., 2007).

530 Combining coagulation process with related techniques such as Fenton's reagent may also be

531   beneficial for trace organic contaminant removal too. However, no such studies could be

532   identified in the literature.

533

534   Removal of trace organic contaminant can be enhanced by utilizing oxidizing agents such as

535   ferrate (hexavalent Fe) which also have coagulating effect (Lee et al., 2009; Lim and Kim,

536   2009; Yang et al., 2011). A small dose of ferrate as a pretreatment could enhance the removal

537   rate of humic acid by traditional coagulants (Lim and Kim, 2009). By using Fe (VI)

538   oxidation-coagulation Lee et al. (2009) achieved 95% removal of diclofenac which compares

539   favourably with the removal efficiency achieved by common coagulants (Carballa et al.,

540   2005). Simultaneous removal of trace organic contaminant and phosphate in secondary

541   treated effluent was achieved by using Fe (VI) (Lee et al., 2009). At a stoichiometric ratio of

542   10:1 (Fe(VI):triclosan), complete removal of triclosan was achieved by Yang et al.(Yang et

543   al., 2011).

544

545   **4.4 Combination with biological reactors**

546   It is very interesting to note that among the compounds listed in Table 3 a few compounds

547   which have been reported to be poorly removed in conventional activated sludge (CAS)

548   process or membrane bioreactor (MBR), have been observed to be significantly removed by

549   coagulation process. For instance, the persistence towards MBR treatment and variable

550   removal of diclofenac (Hai et al., 2011; Hai et al., 2011; Tadkaew et al., 2011) and

551   hydrochlorothiazide (Sipma et al., 2010) are well known. However, these compounds were

552   well removed by coagulation (Table 4). On the other hand, some of the hydrophobic

553   compounds (Log D> 3.2), such as hormones, which are routinely reported to be significantly

554   removed by MBR treatment (Hai et al., 2011; Tadkaew et al., 2011), were poorly removed by

555   coagulation treatment (Table 3). Given the complementary nature of the two treatment

556   processes, it is likely that simultaneous addition of coagulants into MBR in analogy to

557   simultaneous addition of activated carbon (Li et al., 2011) would result in enhanced removal

558   of trace organic contaminant as compared to their standalone applications. Serrano et al.

559   (2010) conducted a preliminary study on direct addition of a coagulant into a CAS reactor for

560   trace organic contaminant removal. On the other hand, the effect of direct addition of

561   coagulant (inorganic or organic or both) into MBR on phosphorous removal by MBR

562   treatment has been explored in a few studies (Nguyen et al., 2010; Song et al., 2008).

563   However, the aspect of trace organic contaminant removal in such systems appears to have

564   not been explored.

565

566   **5. Future scope of research**

567

568   This review highlights the potential for further optimization of the available coagulation

569   techniques to formulate coagulation-based combined processes to enhance the removal of

570   trace organic contaminant. The discussion provided here also emphasizes the need for more

571   fundamental research on the mechanisms of trace organic contaminant removal by various

572   coagulants so as to facilitate the development of high performance new generation coagulants.

573   The effects of the properties of coagulants and target trace organic contaminant (e.g,

574   hydrophobicity, charge, polarizability and presence of specific functional groups) as well as

575   of operational parameters on the trace organic contaminant removal remain poorly studied

576   although their important role is quite apparent.

577

578   The impact of the data collected from the literature reviewed in this study is limited by the

579   amount of research which has been conducted to date focusing on this specific topic. This

580   may be attributed to the relatively recent increase in the scale of water recycling schemes for

581   the augmentation of potable water supplies, and the associated increasing concern regarding

582   the presence of trace organic contaminant. Another reason for the lack of focus on

583   coagulation is that it is generally considered to be an inefficient method of removing trace

584   organic contaminant, and as a result there seems to be a stronger focus on advanced methods

585   of water treatment which have shown to, or are considered to have the potential to be, more

586   efficient methods of removing trace organic contaminant from water. In addition to the

587   limited amount of research in this specific area, the data specifically relating to coagulation

588   was often insufficient to draw meaningful conclusions regarding the effects of coagulant type,

589   dosage and operational parameters. The pH of the water during the coagulation treatment

590   stage was not frequently reported and thus it was not always possible to determine the effects

591   of pH on the removal efficiency.

592

593   Among the available chemical coagulation and flocculation technologies, pre-hydrolyzed

594   coagulants such as PACl, PFCl, PFS and PAFCl are often considered superior to the

595   hydrolyzing metal salts in terms of turbidity and color removal over a wide pH range and

596   requiring smaller dosage. However, the effectiveness of most of the pre-hydrolyzed

597   coagulants for trace organic contaminant removal is yet to be explored. The use of natural

598   coagulants (e.g., polysaccharides, chitosan, guar gum etc.) as coagulant aids to enhance trace

599   organic contaminant removal is another important topic which remains unexplored. Natural

600   coagulants are non-toxic, biodegradable and environmentally friendly and, therefore, are

601   particularly promising considering simultaneous application of coagulants into bioreactor.

602

603   There does not seem to have been any research to date which has focused specifically on the

604   application of new composite coagulants to water treatment for the removal of trace organic

605   contaminant. This represents an important gap in the current research and it is therefore

606   indispensable that future research focus on this area. Given that traditional coagulants have

607   not been designed for the purpose of removing trace organic contaminant, by studying the

608   performance of new types of coagulants under different operating conditions, there is the

609   potential to identify coagulants which may be more effective in removing trace organic

610   contaminant. Research in this area may assist in the evaluation of the merit of efficient hybrid

611   treatment processes combining conventional physicochemical water treatment processes such

612   as coagulation, with biological processes such as MBR, for the removal of trace organic

613   contaminant.

614

615   **6. Conclusion**

616   A comprehensive review of the current literature pertaining to the removal of trace organic

617   contaminant from drinking water and wastewater using coagulation process has been

618   furnished here. The analysis of the data collected from the literature reviewed in this study

619   largely reaffirms the consensus which has been reached to date, that trace organic

620   contaminant tend to be poorly removed by coagulation treatment. The literature does

621   however show that certain musk fragrances and pharmaceutical compounds can be

622   effectively removed using coagulation. An analysis of the removal data for all compounds

623   covered in this review was carried out according to their relative hydrophobicity (Log D).

624   This analysis showed that although hydrophobicity can explain the high removal of certain

625   compounds, there was no discernable correlation between Log D and removal, suggesting

626 that hydrophobicity is not the sole factor governing removal by coagulation, even for

627 significantly hydrophobic compounds. This implies that the usual method of coagulant

628 selection based on turbidity/suspended solids removal may not be always effective.. Pre-

629 coagulation has been found to enhance the trace organic contaminant removal performance of

630 the advanced treatment processes such as ozonation, GAC adsorption and nanofiltration. The

631 research to date has largely focused on traditional coagulants such as ferric and aluminium

632 coagulants which were not designed for the purpose of removing trace organic contaminant.

633 Therefore there is the potential to investigate the efficiency of new generation high

634 performance coagulants in removing trace organic contaminant.

635

641 **References**
642
643 Al-Rifai, J.H., Khabbaz, H., Schäfer, A.I., 2011. Removal of pharmaceuticals and endocrine
644   disrupting compounds in a water recycling process using reverse osmosis systems.
645   Separation and Purification Technology 77, 60-67.
646 Alturki, A.A., Tadkaew, N., McDonald, J.A., Khan, S.J., Price, W.E., Nghiem, L.D., 2010.
647   Combining MBR and NF/RO membrane filtration for the removal of trace organics in
648   indirect potable water reuse applications. Journal of Membrane Science 365, 206-215.
649 Barrera-Díaz, C., Bilyeu, B., Roa, G., Bernal-Martinez, L., 2011. Physicochemical aspects of
650   electrocoagulation. Separation & Purification Reviews 40, 1-24.
651 Belgiorno, V., Rizzo, L., Fatta, D., Della Rocca, C., Lofrano, G., Nikolaou, A., Naddeo, V.,
652   Meric, S., 2007. Review on endocrine disrupting-emerging compounds in urban
653   wastewater: Occurrence and removal by photocatalysis and ultrasonic irradiation for
654   wastewater reuse. Desalination 215, 166-176.
655 Bellona, C., Drewes, J.E., Xu, P., Amy, G., 2004. Factors affecting the rejection of organic
656   solutes during NF/RO treatment—a literature review. Water research 38, 2795-2809.

657   Bodzek, M., Dudziak, M., 2006. Elimination of steroidal sex hormones by conventional
658   water treatment and membrane processes. Desalination 198, 24-32.
659   Boyd, G., 2003. Pharmaceuticals and personal care products (PPCPs) in surface and treated
660   waters of louisiana, USA and ontario, canada. The Science of The Total Environment
661   311, 135-149.
662   Bundy, M.M., Doucette, W. J., McNeill, L., Ericson, J. F., 2007. Removal of pharmaceuticals
663   and related compounds by a bench-scale drinking water treatment system. Journal of
664   Water Supply: Research and Technology - AQUA 56, 105-115.
665   Carballa, M., Omil, F., Lema, J.M., 2003. Removal of pharmaceuticals and personal care
666   products (PPCPs) from municipal wastewaters by physico-chemical processes.
667   Electronic Journal of Environmental, Agricultural and Food Chemistry 2, 309-313.
668   Carballa, M., Omil, F., Lema, J.M., 2005. Removal of cosmetic ingredients and
669   pharmaceuticals in sewage primary treatment. Water Research 39, 4790-4796.
670   Carlsson, C., Johansson, A.-K., Alvan, G., Bergman, K., Kühler, T., 2006. Are
671   pharmaceuticals potent environmental pollutants?: Part ii: Environmental risk
672   assessments of selected pharmaceutical excipients. Science of The Total Environment
673   364, 88-95.
674   Chang, S., Waite, T.D., Ong, P.E.A., Schafer, A.I., Fane, A.G., 2004. Assessment of trace
675   estrogenic contaminants removal by coagulant addition, powdered activated carbon
676   adsorption and powdered activated carbon/microfiltration processes. Journal of
677   Environmental Engineering 130, 736-742.
678   Chen, T., Gao, B., Yue, Q., 2010. Effect of dosing method and pH on color removal
679   performance and floc aggregation of polyferric chloride–polyamine dual-coagulant in
680   synthetic dyeing wastewater treatment. Colloids and Surfaces A: Physicochemical and
681   Engineering Aspects 355, 121-129.
682   Choi, K.J., Kim, S.G., Kim, S.H., 2008. Removal of antibiotics by coagulation and granular
683   activated carbon filtration. Journal of hazardous materials 151, 38-43.
684   Choi, K.J., Kim, S.G., Kim, C. W., Park, J. K., 2006. Removal efficiencies of endocrine
685   disrupting chemicals by coagulation-flocculation, ozonation, powdered-granular
686   activated carbon adsorption, and chlorination. Korean Journal of Chemical
687   Engineering 23, 399-408.
688   Ciardelli, G., Ranieri, N., 2001. The treatment and reuse of wastewater in the textile industry
689   by means of ozonation and electroflocculation. Water Research 35, 567-572.
690   Cirja, M., Ivashechkin, P., Schäffer, A., Corvini, P., 2008. Factors affecting the removal of
691   organic micropollutants from wastewater in conventional treatment plants (CTP) and
692   membrane bioreactors (MBR). Reviews in Environmental Science and Biotechnology
693   7, 61-78.
694   Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N., Kroiss, H., 2005. Removal of
695   selected pharmaceuticals, fragrances and endocrine disrupting compounds in a
696   membrane bioreactor and conventional wastewater treatment plants. Water research
697   39, 4797-807.
698   Comerton, A.M., Andrews, R.C., Bagley, D.M., Hao, C., 2008. The rejection of endocrine
699   disrupting and pharmaceutically active compounds by NF and RO membranes as a
700   function of compound and water matrix properties. Journal of Membrane Science
701   313, 323-335.

702 Daughton, C., Ternes, T., 1999. Pharmaceuticals and personal care products in the
703   environment: Agents of subtle change? Environmental Health Perspective 107, 907-
704   938.
705 de Ridder, D.J., Villacorte, L., Verliefde, A.R.D., Verberk, J.Q.J.C., Heijman, S.G.J., Amy,
706   G.L., van Dijk, J.C., 2010. Modeling equilibrium adsorption of organic
707   micropollutants onto activated carbon. Water Research 44, 3077-3086.
708 Dempsey, B.A., O'Melia, C.R., 1984. Removal of naturally occurring compounds by
709   coagulation and sedimentation. Critical Reviews in Environmental Control 14, 311-
710   331.
711 Duan, J., Gregory, J., 2003. Coagulation by hydrolysing metal salts. Advances in Colloid and
712   Interface Science 100–102, 475-502.
713 Gao, B., Yue, Q., Miao, J., 2003. Evaluation of polyaluminium ferric chloride (PAFC) as a
714   composite coagulant for water and wastewater treatment. Water Science and
715   Technology, pp. 127-132.
716 Grover, D.P., Zhou, J.L., Frickers, P.E., Readman, J.W., 2011. Improved removal of
717   estrogenic and pharmaceutical compounds in sewage effluent by full scale granular
718   activated carbon: Impact on receiving river water. Journal of Hazardous Materials
719   185, 1005-1011.
720 Haberhauer, G., Pfeiffer, L., Gerzabek, M.H., 2000. Influence of molecular structure on
721   sorption of phenoxyalkanoic herbicides on soil and its particle size fractions. Journal
722   of Agricultural and Food Chemistry 48, 3722-3727.
723 Hai, F.I., Tadkaew, N., McDonald, J.A., Khan, S.J., Nghiem, L.D., 2011. Is halogen content
724   the most important factor in the removal of halogenated trace organics by mbr
725   treatment? Bioresource Technology 102, 6299-6303.
726 Hai, F.I., Tessmer, K., Nguyen, L.N., Kang, J., Price, W.E., Nghiem, L.D., 2011. Removal of
727   micropollutants by membrane bioreactor under temperature variation. Journal of
728   Membrane Science 383, 144-151.
729 Hai, F.I., Yamamoto, K., 2011. Membrane biological reactors. in: P. Wilderer (Ed.) Treatise
730   on water science. Elsevier, Oxford, pp. 571-613.
731 Hai, F.I., Yamamoto, K., Fukushi, K., 2007. Hybrid treatment systems for dye wastewater.
732   Critical Reviews in Environmental Science and Technology 37, 315-377.
733 Hoeger, B., Köllner, B., Dietrich, D.R., Hitzfeld, B., 2005. Water-borne diclofenac affects
734   kidney and gill integrity and selected immune parameters in brown trout (Salmo trutta
735   f. fario). Aquatic Toxicology 75, 53-64.
736 Huerta-Fontela, M., Galceran, M.T., Ventura, F., 2011. Occurrence and removal of
737   pharmaceuticals and hormones through drinking water treatment. Water research 45,
738   1432-42.
739 Huerta-Fontela, M.G., M. T.; Ventura, F., 2008. Stimulatory drugs of abuse in surface waters
740   and their removal in a conventional drinking water treatment plant. Environmental
741   Science & Technology 42, 6809-6816.
742 Joseph, L., Zaib, Q., Khan, I.A., Berge, N.D., Park, Y.-G., Saleh, N.B., Yoon, Y., 2011.
743   Removal of bisphenol a and 17α-ethinyl estradiol from landfill leachate using single-
744   walled carbon nanotubes. Water Research 45, 4056-4068.
745 Kim, Y., Choi, K., Jung, J., Park, S., Kim, P.-G., Park, J., 2007a. Aquatic toxicity of
746   acetaminophen, carbamazepine, cimetidine, diltiazem and six major sulfonamides,
747   and their potential ecological risks in korea. Environment International 33, 370-375.

748 Kim, S.D., Cho, J., Kim, I.S., Vanderford, B.J., Snyder, S.A., 2007b. Occurrence and
749   removal of pharmaceuticals and endocrine disruptors in south korean surface,
750   drinking, and waste waters. Water research 41, 1013-21.
751 Kimura, K., Hara, H., Watanabe, Y., 2005. Removal of pharmaceutical compounds by
752   submerged membrane bioreactors (MBRs). Desalination 178, 135-140.
753 Kolok, A.S., Snow, D.D., Kohno, S., Sellin, M.K., Guillette Jr, L.J., 2007. Occurrence and
754   biological effect of exogenous steroids in the elkhorn river, nebraska, USA. Science
755   of The Total Environment 388, 104-115.
756 Lai, H.-T., Hou, J.-H., Su, C.-I., Chen, C.-L., 2009. Effects of chloramphenicol, florfenicol,
757   and thiamphenicol on growth of algae chlorella pyrenoidosa, isochrysis galbana, and
758   tetraselmis chui. Ecotoxicology and Environmental Safety 72, 329-334.
759 Lai, K.M., Johnson, K.L., Scrimshaw, M.D., Lester, J.N., 2000. Binding of waterborne
760   steroid estrogens to solid phases in river and estuarine systems. Environmental
761   Science & Technology 34, 3890-3894.
762 Le-Clech, P., Chen, V., Fane, T.A.G., 2006. Fouling in membrane bioreactors used in
763   wastewater treatment. Journal of Membrane Science 284, 17-53.
764 Le-Minh, N., Khan, S.J., Drewes, J.E., Stuetz, R.M., 2010. Fate of antibiotics during
765   municipal water recycling treatment processes. Water Research 44, 4295-4323.
766 Leckie, J., Sun, D., Robertson, A.P., 2004. Membrane-coagulation reactor for water treatment.
767   Stanford University.
768 Lee, Y., Zimmermann, S.G., Kieu, A.T., von Gunten, U., 2009. Ferrate (Fe(VI)) application
769   for municipal wastewater treatment: A novel process for simultaneous micropollutant
770   oxidation and phosphate removal. Environmental Science & Technology 43, 3831-
771   3838.
772 Lefebvre, O., Lee, L.Y., Ng, H.Y., 2010. Physico-chemical treatment of micropollutants:
773   Coagulation and membrane processes. in: J. Virkutyte, Jegatheesan, V., Varma, R. S.
774   (Ed.) Treatments of micropollutants in water and wastewater. IWA Publishing,
775   London, pp. 205-237.
776 Leiknes, T., 2009. The effect of coupling coagulation and flocculation with membrane
777   filtration in water treatment: A review. Journal of Environmental Sciences 21, 8-12.
778 Li, X., Hai, F.I., Nghiem, L.D., 2011. Simultaneous activated carbon adsorption within a
779   membrane bioreactor for an enhanced micropollutant removal. Bioresource
780   Technology 102, 5319-5324.
781 Lia, T., Zhua, Z., Wanga, D., Yaob, C., Tang, H., 2006. Characterization of floc size, strength
782   and structure under various coagulation mechanisms. Powder Technology 168, 104-
783   110.
784 Lim, M., Kim, M.-J., 2009. Removal of natural organic matter from river water using
785   potassium ferrate (vi). Water, Air, & Soil Pollution 200, 181-189.
786 Luckenbach, T., Epel, D., 2005. Nitromusk and polycyclic musk compounds as long-term
787   inhibitors of cellular xenobiotic defense systems mediated by multidrug transporters.
788   Environmental Health Perspectives 113, 17-24.
789 Lyssimachou, A., Arukwe, A., 2007. Alteration of brain and interrenal StAR protein, P450scc,
790   and Cyp11beta mRNA levels in atlantic salmon after nominal waterborne exposure to
791   the synthetic pharmaceutical estrogen ethynylestradiol. Journal of Toxicology and
792   Environmental Health 70, 606 - 613.
793 Martins, A.F., Mallmann, C.A., Arsand, D.R., Mayer, F.M., Brenner, C.G.B., 2011.
794   Occurrence of the antimicrobials sulfamethoxazole and trimethoprim in hospital

795   effluent and study of their degradation products after electrocoagulation. CLEAN –
796   Soil, Air, Water 39, 21-27.
797 Matilainen, A., Vepsäläinen, M., Sillanpää, M., 2010. Natural organic matter removal by
798   coagulation during drinking water treatment: A review. Advances in Colloid and
799   Interface Science 159, 189-197.
800 Muller, S., Uhi, W., 2009. Influence of hybrid coagulation-ultrafiltration pretreatment on
801   trace organics adsorption in drinking water treatment. Journal of Water Supply
802   Research and Technology-Aqua 58, 170-180.
803 Nghiem, L.D., Manis A., Soldenhoff, K., Schäfer, A.I., 2004. Estrogenic hormone removal
804   from wastewater using NF/RO membranes. Journal of Membrane Science 242, 37-45.
805 Nghiem, L.D., Schäfer, A.I., Waite, T.D., 2003. Membrane filtration in water recycling:
806   Removal of natural hormones. Water Supply 3, 155-160.
807 Nguyen, L.N., Hai, F.I., Kang, J., Price, W.E., Nghiem, L.D., 2011. Removal of trace organic
808   contaminants by a membrane bioreactor – granular activated carbon (MBR–GAC)
809   system. Bioresource Technology doi:10.1016/j.biortech.2011.10.051.
810 Nguyen, T.T., Guo, W., Ngo, H.H., Vigneswaran, S., 2010. A new combined inorganic-
811   organic flocculant (CIOF) as a performance enhancer for aerated submerged
812   membrane bioreactor. Separation and Purification Technology 75, 204-209.
813 Ottinger, M.A., Abdelnabi, M., Quinn, M., Golden, N., Wu, J., Thompson, N., 2002.
814   Reproductive consequences of EDCs in birds: What do laboratory effects mean in
815   field species? . Neurotoxicology and Teratology 24, 17-28.
816 Pal, A., Gin, K.Y.H., Lin, A.Y.C., Reinhard, M., 2010. Impacts of emerging organic
817   contaminants on freshwater resources: Review of recent occurrences, sources, fate
818   and effects. Science of the Total Environment 408, 6062-6069.
819 Papic, S., Koprivanac, N., Loncaric Bozic, A., Metes, A., 2004. Removal of some reactive
820   dyes from synthetic wastewater by combined Al(III) coagulation/carbon adsorption
821   process. Dyes and Pigments 62, 291-298.
822 Pomati, F., Castiglioni, S., Zuccato, E., Fanelli, R., Vigetti, D., Rossetti, C., 2006. Effects of a
823   complex mixture of therapeutic drugs at environmental levels on human embryonic
824   cells. Environmental Science & Technology 40, 2442.
825 Purdom, C.E., Hardiman, P.A., Bye, V.J., Eno, N.C., Tyler, C.R., Sumpter, J.P., 1994.
826   Estrogenic effects of effluents from sewage treatment works. Journal of Chemistry
827   and Ecology 8, 275-285.
828 Radcliffe, J.C., 2006. Future directions for water recycling in australia. Desalination 187, 77-
829   87.
830 Rebhun, M., Meir, S., Laor, Y., 1998. Using dissolved humic acid to remove hydrophobic
831   contaminants from water by complexation−flocculation process. Environmental
832   Science & Technology 32, 981-986.
833 Rojas, M.R., Leung, C., Whitley, D., Zhu, Y., Arnold, R.G., Sáez, A.E., 2011. Advanced
834   oxidation of trace organics in water by hydrogen peroxide solar photolysis. Industrial
835   & Engineering Chemistry Research 50, 12479-12487.
836 Serrano, D., Lema, J.M., Omil, F., 2010. Influence of the employment of adsorption and
837   coprecipitation agents for the removal of ppcps in conventional activated sludge (CAS)
838   systems. Water Science & Technology 63, 728-735.
839 Sipma, J., Osuna, B., Collado, N., Monclús, H., Ferrero, G., Comas, J., Rodriguez-Roda, I.,
840   2010. Comparison of removal of pharmaceuticals in mbr and activated sludge systems.
841   Desalination 250, 653-659.

842 Snoeyink, V.L., Chen, A.S.C., 1985. Removal of organic micropollutants by coagulation and
843   adsorption. Science of The Total Environment 47, 155-167.
844 Song, K.-G., Kim, Y., Ahn, K.-H., 2008. Effect of coagulant addition on membrane fouling
845   and nutrient removal in a submerged membrane bioreactor. Desalination 221, 467-
846   474.
847 Stackelberg, P.E., Gibs, J., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Lippincott, R.L., 2007.
848   Efficiency of conventional drinking-water-treatment processes in removal of
849   pharmaceuticals and other organic compounds. The Science of The Total
850   Environment 377, 255-72.
851 Suarez, S., Lema, J.M., Omil, F., 2009. Pre-treatment of hospital wastewater by coagulation-
852   flocculation and flotation. Bioresource technology 100, 2138-46.
853 Tadkaew, N., Hai, F.I., McDonald, J.A., Khan, S.J., Nghiem, L.D., 2011. Removal of trace
854   organics by mbr treatment: The role of molecular properties. Water Research, 2439-
855   2451.
856 Ternes, T.A., M. Meisenheimer, et al., 2002. Removal of pharmaceuticals during drinking
857   water treatment. Environmental Science & Technology 36, 3855-3863.
858 Thuy, P.T., Moons, K., van Dijk, J.C., Anh, V.N., Van der Bruggen, B., 2008. To what extent
859   are pesticides removed from surface water during coagulation-flocculation? Water
860   and Environment Journal 22, 217-223.
861 Tomaszewska, M., Mozia, S., Morawski, A.W., 2004. Removal of organic matter by
862   coagulation enhanced with adsorption on PAC. Desalination 161, 79-87.
863 Tuhkanen, T.A., Marinosa, P.C., 2010. UV irradiation for micropollutant removal from
864   aqueous solutions in the presence of H_2O_2. in: J. Virkutyte, Jegatheesan, V., Varma, R.
865   S. (Ed.) Treatments of micropollutants in water and wastewater. IWA Publishing,
866   London, pp. 295-316.
867 Upadhyayula, V.K.K., Deng, S., Mitchell, M.C., Smith, G.B., 2009. Application of carbon
868   nanotube technology for removal of contaminants in drinking water: A review.
869   Science of The Total Environment 408, 1-13.
870 Verma, A.K., Dash, R.R., Bhunia, P., 2012. A review on chemical coagulation/flocculation
871   technologies for removal of colour from textile wastewaters. Journal of
872   Environmental Management 93, 154-168.
873 Vieno, N., Tuhkanen, T., Kronberg, L., 2006. Removal of pharmaceuticals in drinking water
874   treatment: Effect of chemical coagulation Environmental Technology 27, 183-192.
875 Vieno, N.M., H. Härkki, et al., 2007. Occurrence of pharmaceuticals in river water and their
876   elimination in a pilot-scale drinking water treatment plant. Environmental Science &
877   Technology 41, 5077-5084.
878 Visvanathan, C., Ben Aim, R., Parameshwaran, K., 2000. Membrane separation bioreactors
879   for wastewater treatment. Critical Reviews in Environmental Science and Technology
880   30, 1-48.
881 Wang, D.S., Wu, X.H., Huang, L., Tang, H.X., Qu, J.H., 2007. Nano-inorganic polymer
882   flocculant: From theory to practice. . in: H.H. Hahn, Hoffman, E., Odegaard, H. (Ed.)
883   Chemical water and wastewater treatment. IWA Publishing, London, pp. 181-188.
884 Wells, M.J., 2006. Log Dow: Key to understanding and regulating wastewater-derived
885   contaminants. Environmental Chemistry 3, 439-449.
886 Westerhoff, P., Yoon, Y., Snyder, S., Wert, E., 2005. Fate of endocrine-disruptor,
887   pharmaceutical, and personal care product chemicals during simulated drinking water
888   treatment processes. Environmental Science & Technology 39, 6649-6663.

889   Wright, J.M., Schwartz, J., Dockery, D.W., 2004. The effect of disinfection by-products and
890   mutagenic activity on birth weight and gestational duration. Environmental Health
891   Perspectives 112, 920-925.
892   Yan, M., Wang, D., Qu, J., He, W., Chow, C.W.K., 2007. Relative importance of hydrolyzed
893   Al(III) species (Al$_a$, Al$_b$, and Al$_c$) during coagulation with polyaluminum chloride: A
894   case study with the typical micro-polluted source waters. Journal of Colloid and
895   Interface Science 316, 482-489.
896   Yan, M., Wang, D., Yu, J., Ni, J., Edwards, M., Qu, J., 2008. Enhanced coagulation with
897   polyaluminum chlorides: Role of pH/alkalinity and speciation. Chemosphere 71,
898   1665-1673.
899   Yang, B., Ying, G.-G., Zhao, J.-L., Zhang, L.-J., Fang, Y.-X., Nghiem, L.D., 2011. Oxidation
900   of triclosan by ferrate: Reaction kinetics, products identification and toxicity
901   evaluation. Journal of Hazardous Materials 186, 227-235.
902   Yang, K., Li, Z., Zhang, H., Qian, J., Chen, G., 2010. Municipal wastewater phosphorus
903   removal by coagulation. Environmental Technology 31, 601-609.
904   Yu, Y., Zhuang, Y.Y., Li, Y., Qiu, M.Q., 2002. Effect of dye structure on the interaction
905   between organic flocculant PAN-DCD and dye. Industrial and Engineering Chemistry
906   Research 41, 1589-1596.
907   Zaisheng, Y., Shihe, W., Xiaokun, K., Yu, M., 2009. Pilot-scale hybrid
908   coagulation/membrane bioreactor (HCMBR) for textile dyeing wastewater advanced
909   treatment. Proceedings in the Bioinformatics and Biomedical Engineering, ICBBE,
910   3rd International Conference, 1-4.
911   Zhang, L.Z., Chen, X.D., Ma, J., Yu, M., Li, X., 2011. Effects on phenol removal in the
912   process of enhanced coagulation by manganese dioxide formed in situ. Huanjing
913   Kexue/Environmental Science 32, 2926-2930.
914   Zhao, H., Hu, C., Liu, H., Zhao, X., Qu, J., 2008. Role of aluminum speciation in the removal
915   of disinfection byproduct precursors by a coagulation process. Environmental Science
916   & Technology 42, 5752-5758.
917   Zhou, T., 2011. Removal of organic micropollutants by coagulation in wastewater treatment.
918   Masters thesis, Department of Water Management. Delft University of Technology,
919   Delft.
920   Zorita, S., Mårtensson, L., Mathiasson, L., 2009. Occurrence and removal of pharmaceuticals
921   in a municipal sewage treatment system in the south of sweden. Science of the Total
922   Environment 407, 2760-2770.
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924
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Figure caption

Figure 1: Plot of removal efficiency and Log D (at pH 7) of the compounds listed in Table 3 showing no apparent relationship between hydrophobicity and removal by coagulation treatment. A similar trend was observed when the graph was re-plotted with the Log D values at a pH of 5. Log D data were obtained from SciFinder database (https://scifinder.cas.org/scifinder/view/scifinder/scifinderExplore.jsf)
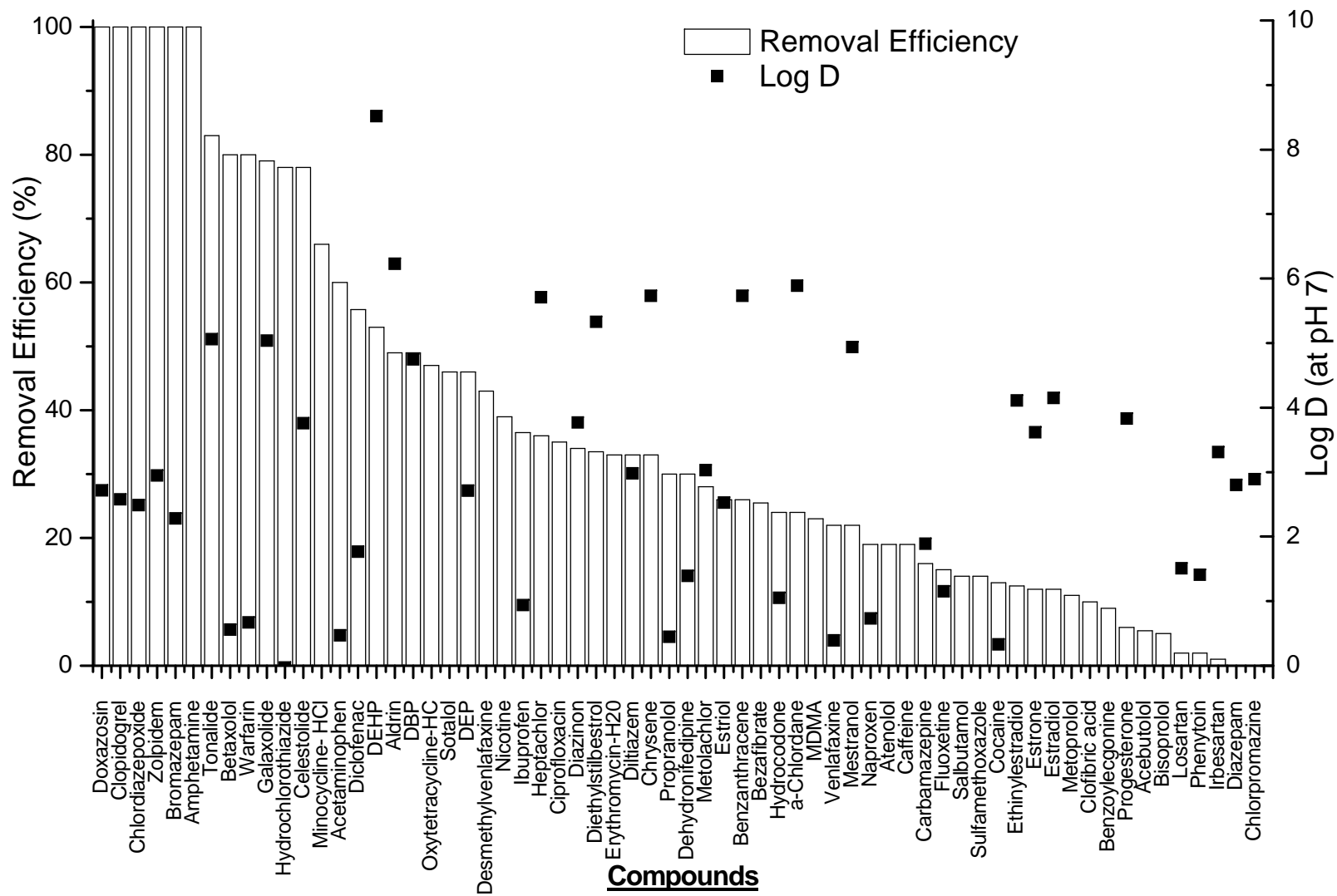
Figure 1

Table 1: Toxicological effect of trace organics in water on human and aquatic organisms as reported in selected studies (modified after Pal et al. (2010))

Compound type	Compounds causing risks	Concentration of exposure	Type of risks involved	Reference
Hormone/ steroid	Ethinylestradiol, zearalonol, 17 β trenbolone and melengestrol acetate	< 1-68 ng/ L	Different levels of hepatic gene expression in freshwater fish fathead minnows.	(Kolok et al., 2007)
Hormone/ steroid	17 α-ethinylestradiol	5- 50 ng/ L	Modulation of brain and inter-renal steroidogenic acute regulatory protein and cytochrome P-450 mediated cholesterol side chain cleavage expressions of juvenile salmon were modulated with time and concentration	(Lyssimachou and Arukwe, 2007)
Disinfection by-products	Chloroform, BDCM, dibromochloromethane and bromoform	20-160 µg /L	Reductions in mean birth weight; increases in gestational duration and a reduced risk of preterm delivery of human baby	(Wright et al., 2004)
Musk fragrances	Nitro- and polycyclic musks	0.09-2.56 µM	Inhibit the activity of multidrug efflux transporters responsible for multixenobiotic resistance (MXR) in gills of the marine mussel *Mytilus californianus*	(Luckenbach and Epel, 2005)
Pharmaceutical	Diclofenac	0.5 -50 µg/ L	Affect tissues of gills and kidney of freshwater fish brown trout	(Hoeger et al., 2005)
Pharmaceutical	Ibupforen, diclofenac	0.01 µg/ L	Risk to aquatic environment with chronic toxic effect (such as inhibited polyp regeneration and reduced reproduction)	(Carlsson et al., 2006)
Pharmaceutical	Mixture of 13[a] pharmaceuticals	10 -1000 ng/ L	Inhibited growth of human embryonic kidney cells HEK293 with the highest effect observed as a 30% decrease in cell proliferation compared to control	(Pomati et al., 2006)
Pharmaceutical	Diltiazem, acetaminophen and sulfamethoxazole	8.2 – 271.3 µg/ L	Diltiazem proved to be most toxic with a lethal conc. of 8.2 mg/L for freshwater invertebrate *Daphnia magna*	(Kim et al. 2007a)
Pharmaceutical	Chloramphenicol, florfenicol and thiamphenicol	1.3 – 158 mg/ L	Inhibited growth of freshwater *Chlorella pyrenoidosa* and marine *Isochrysis galbana* and *Tetraselmis chui*	(Lai et al., 2009)

[a]atenolol, bezafibrate, carbamazepine, cyclophosphamide, ciprofloxacin, furosemide, hydrochlorothiazide, ibuprofen, lincomycin, ofloxacin, ranitidine, salbutamol, and sulfamethoxazole

Table 2: Available technologies for trace organics removal from water and wastewater

Process	Advantages	Disadvantages	Reference
Chemical coagulation	An economical conventional treatment process widely used for turbidity and color removal	Produces large quantity of sludge; the available coagulants were not developed aiming at trace organics removal, therefore, removes only selected groups of trace organics	(Duan and Gregory, 2003; Huerta-Fontela et al., 2011; Lefebvre et al., 2010; Matilainen et al., 2010; Verma et al., 2012; Vieno, 2007)
Electrocoagulation	Potential of achieving both adsorption and degradation and removal of both soluble and insoluble organics	Inherent limitations are secondary pollution (from chlorinated organics, heavy metals) and high cost (electricity); compound-specific removal has been reported by the few available references regarding trace organics removal	(Barrera-Díaz et al., 2011; Martins et al., 2011)
Activated carbon adsorption	Well-established tertiary treatment option; removal of wide variety of trace organics	Competitive adsorption leads to early breakthrough of several groups of compounds; difficult regeneration and costly disposal of potentially hazardous spent adsorbent	(Grover et al., 2011; Nguyen et al., 2011; Ternes, 2002)
Nanofiltration/ Reverse osmosis	Good removal of a large range of trace organics via size exclusion and electrostatic repulsion	A considerable degree of complexity associated with the separation process; production of concentrated sludge; adsorption to membrane surface and subsequent diffusion of the hydrophobic organics through the membrane	(Alturki et al., 2010; Bellona et al., 2004; Nghiem et al., 2004)
Advanced oxidation processes	Degradation of various trace organics by generation of a large number of highly reactive free radicals, surpassing the conventional oxidants by far in efficiency	Pretreatment almost always necessary to remove suspended solids, radical scavengers and competing ions; formation of toxic by-products; expensive, and very few full scale plants	(Belgiorno et al., 2007; Rojas et al., 2011; Tuhkanen and Marinosa, 2010)
Membrane bioreactor (MBR)	Excellent removal of significantly hydrophobic trace organics in a single-step compact biological process	Inefficient removal of hydrophilic and persistent trace organics requiring a polishing step	(Cirja et al., 2008; Li et al., 2011; Tadkaew et al., 2011)

Table 3   Summary of available data regarding trace organics removal by coagulation/flocculation

Category	Compound Class	Compound	Removal (%)	Coagulant Type	Coagulant Dose	pH	Reference
Pharmaceuticals	Analgesic	Hydrocodone	24	$Al_2(SO_4)_3$	78 mg/L	6.8	(Westerhoff et al., 2005)
	Analgesic	Acetaminophen	60	$FeCl_3$	20-45 mg/L	4.5-5.5	(Stackelberg et al., 2007)
	Anti-inflammatory	Diclofenac	8-77	$Fe_2(SO_4)_3$	94 mg/L	4.5-4.9	(Vieno et al., 2006; Vieno, 2007)
	Anti-inflammatory	Diclofenac	11	$FeCl_3$	25 mg/L	7.9-8.5	(Suarez et al., 2009; Ternes, 2002)
	Anti-inflammatory	Diclofenac	>65	$Al_2(SO_4)_3$, $FeCl_3$	50 mg/L	--	(Carballa et al., 2005)
	Anti-inflammatory	Diclofenac	<25	$FeCl_3$	0.07 mg/L	--	(Zorita et al., 2009)
	Anti-inflammatory	Diclofenac	70	PACl	200 mg/L	--	(Carballa et al., 2003)
	Anti-inflammatory	Naproxen	10	$Fe_2(SO_4)_3$	94 mg/L	4.9	(Vieno, 2007)
	Anti-inflammatory	Naproxen	5	$Al_2(SO_4)_3$	--	--	(Boyd, 2003)
	Anti-inflammatory	Naproxen	42	$FeCl_3$	25 mg/L	7.9-8.5	(Suarez et al., 2009)
	Anti-inflammatory	Naproxen	20	$FeCl_3$	50 mg/L	--	(Carballa et al., 2005)
	Anti-inflammatory	Naproxen	<25	$FeCl_3$	0.07 mg/L	--	(Zorita et al., 2009)
	Anti-inflammatory	Ibuprofen	23	$FeCl_3$	25 mg/L	7.9-8.5	(Suarez et al., 2009)
	Anti-inflammatory	Ibuprofen	50	$Fe_2(SO_4)_3$	140 μmol/L	4.5	(Vieno et al., 2006)
	Anti-inflammatory	Ibuprofen	<25	$FeCl_3$	0.07 mg/L	--	(Zorita et al., 2009)
	Antibiotic	Sulfamethoxazole	0-33	$FeCl_3$	20-45 mg/L	4.5-5.5	(Stackelberg et al., 2007; Suarez et al., 2009)
	Antibiotic	Sulfamethoxazole	< 10	$Fe_2(SO_4)_3$	140 μmol/L	4.5	(Vieno et al., 2006)
	Antibiotic	Ciprofloxacin	35	$Fe_2(SO_4)_3$	94 mg/L	4.9	(Vieno, 2007)
	Antibiotic	Oxytetracycline-HC	47	PACl	40 mg/L	7.4	(Choi et al., 2008)

Table 3   Summary of available data regarding trace organics removal by coagulation/flocculation

Category	Compound Class	Compound	Removal (%)	Coagulant Type	Coagulant Dose	pH	Reference
Pharmaceuticals	Antibiotic	Minocycline- HCl	66	PACl	40 mg/L	7.4	(Choi et al., 2008)
	Antibiotic	DXC	39	PACl	40 mg/L	7.4	(Choi et al., 2008)
	Antibiotic	Meclocycline-sulfosalicylate (MCC)	57	PACl	40 mg/L	7.4	(Choi et al., 2008)
	Antibiotic	Chlortetracycline (CTC)	55	PACl	40 mg/L	7.4	(Choi et al., 2008)
	Antibiotic	Democlocycline-HCl (DMC)	65	PACl	40 mg/L	7.4	(Choi et al., 2008)
	Antibiotic	Tetracycline (TC)	49	PACl	40 mg/L	7.4	(Choi et al., 2008)
	Antibiotic	Trivofloxacin mesylate	0	$Al_2(SO_4)_3$	25 mg/L	8	(Bundy, 2007)
	Antibiotic	Erythromycin-H20	33	$Al_2(SO_4)_3$	78 mg/L	6.8	(Westerhoff et al., 2005)
	Beta-blocker	Doxazosin	100	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Beta-blocker	Betaxolol	80	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Beta-blocker	Sotalol	46	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Beta-blocker	Propanolol	30	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Beta-blocker	Bisoprolol	5	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Beta-blocker	Atenolol	19	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Beta-blocker	Acebutolol	3	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Beta-blocker	Acebutolol	8	$Fe_2(SO_4)_3$	94 mg/L	4.9	(Vieno, 2007)
	Beta-blocker	Metaprolol	11	$Fe_2(SO_4)_3$	94 mg/L	4.9	(Vieno, 2007)

Table 3　　　　　Summary of available data regarding trace organics removal by coagulation/flocculation

Category	Compound Class	Compound	Removal (%)	Coagulant Type	Coagulant Dose	pH	Reference
Pharmaceuticals	Cardiac	Clopidogrel	100	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Cardiac	Hydrochlorothiazide	78	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Cardiac	Diltiazem	33	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Cardiac	Warfarin	80	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Cardiac	Dehydronifedipine	30	$FeCl_3$	20-45 mg/L	4.5-5.5	(Stackelberg et al., 2007)
	Psychiatric	Chlordiazepoxide	100	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Psychiatric	Zolpidem	100	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Psychiatric	Bromazepam	100	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Psychiatric	Venlafaxine	22	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Psychiatric	Phenytoin	2	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Psychiatric	Diazepam	0	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Psychiatric	Diazepam	0	$FeCl_3$	25 mg/L	7.9-8.5	(Suarez et al., 2009)
	Psychiatric	Desmethylvenlafaxine	43	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Psychiatric	Chlorpromazine	0	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Psychiatric	Carbamaz epoxide	15	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Psychiatric	Carbamazepine	30	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Psychiatric	Carbamazepine	7	$Fe_2(SO_4)_3$	94 mg/L	4.5-4.9	(Vieno et al., 2006; Vieno, 2007)
	Psychiatric	Carbamazepine	12	$FeCl_3$	25 mg/L	7-8.5	(Suarez et al., 2009; Ternes, 2002)

Table 3   Summary of available data regarding trace organics removal by coagulation/flocculation

Category	Compound Class	Compound	Removal (%)	Coagulant Type	Coagulant Dose	pH	Reference
	Psychiatric	Fluoxetine	15	$Al_2(SO_4)_3$	78 mg/L	6.8	(Westerhoff et al., 2005)
	Stimulant	Caffeine	0-38	$Al_2(SO_4)_3$	25-78 mg/L	6.8-8	(Bundy, 2007; Huerta-Fontela, 2008; Westerhoff et al., 2005)
	Stimulant	Cocaine	13	$Al_2(SO_4)_3$	--	--	(Huerta-Fontela, 2008)
	Stimulant	Benzoylecgonine	9	$Al_2(SO_4)_3$	--	--	(Huerta-Fontela, 2008)
	Stimulant	Amphetamine	100	$Al_2(SO_4)_3$	--	--	(Huerta-Fontela, 2008)
	Stimulant	MDMA	23	$Al_2(SO_4)_3$	--	--	(Huerta-Fontela, 2008)
	Stimulant	Nicotine	39	$Al_2(SO_4)_3$	--	--	(Huerta-Fontela, 2008)
Pharmaceuticals	Pulmonary drug	Losartan	2	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Pulmonary drug	Irbesartan	1	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Pulmonary drug	Salbutamol	14	$Al_2(SO_4)_3$	--	7.4-8.5	(Huerta-Fontela et al., 2011)
	Hypolipidemic agent	Bezafibrate	15	$FeCl_3$	40 mg/L	7.5	(Ternes, 2002)
	Hypolipidemic agent	Bezafibrate	36	$Fe_2(SO_4)_3$	140 µmol/L	4.5	(Vieno et al., 2006)
		Tonalide	83	$FeCl_3$	25 mg/L	7.9-8.5	(Suarez et al., 2009)

Table 3 Summary of available data regarding trace organics removal by coagulation/flocculation

Category	Compound Class	Compound	Removal (%)	Coagulant Type	Coagulant Dose	pH	Reference
Musk fragrances		Tonalide	71	PACl	17.5 % w/w	--	(Carballa et al., 2005)
		Tonalide	70	PACl	200 mg/L	--	Carballa, Omil et al. 2003)
		Tonalide	90	FeCl$_3$	75 mg/L	--	(Serrano et al., 2010)
		Galaxolide	79	FeCl$_3$	25 mg/L	7.9-8.5	(Suarez et al., 2009)
		Galaxolide	63	PACl	17.5 % w/w	--	(Carballa et al., 2005)
Musk fragrances		Galaxolide	65	PACl	200 mg/L	--	(Carballa et al., 2003)
		Galaxolide	90	FeCl$_3$	75 mg/L	--	(Serrano et al., 2010)
		Celestolide	78	FeCl$_3$	25 mg/L	7.9-8.5	(Suarez et al., 2009)
Hormone	Estrogen	Estrone	12	Fe$_2$(SO$_4$)$_3$	12.2 mg/L	6.8-7.2	(Bodzek and Dudziak, 2006)
	Estrogen	Estrone	18	PACl	5.4 mg/L	6.8-7.2	(Bodzek and Dudziak, 2006)
	Estrogen	Estrone	5	Al$_2$(SO$_4$)$_3$	78 mg/L	6.8	(Westerhoff et al., 2005)
	Estrogen	Estradiol	17	Fe$_2$(SO$_4$)$_3$	12.2 mg/L	6.8-7.2	(Bodzek and Dudziak, 2006)
	Estrogen	Estradiol	16	PACl	5.4 mg/L	6.8-7.2	(Bodzek and Dudziak, 2006)
	Estrogen	Estradiol	0-2	Al$_2$(SO$_4$)$_3$	25-78 mg/L	6.8-8	(Bundy, 2007; Westerhoff et al., 2005)
	Estrogen	Estriol	21	Fe$_2$(SO$_4$)$_3$	12.2 mg/L	6.8-7.2	(Bodzek and Dudziak, 2006)
	Estrogen	Estriol	31	PACl	5.4 mg/L	6.8-7.2	(Bodzek and Dudziak, 2006)
	Estrogen	Ethinylestradiol	4	Fe$_2$(SO4)$_3$	12.2 mg/L	6.8-7.2	(Bodzek and Dudziak, 2006)
	Estrogen	Ethinylestradiol	21	PACl	5.4 mg/L	6.8-7.2	(Bodzek and Dudziak, 2006)
	Estrogen	Mestranol	10	Fe$_2$(SO4)$_3$	12.2 mg/L	6.8-7.2	(Bodzek and Dudziak, 2006)
	Estrogen	Mestranol	34	PACl	5.4 mg/L	6.8-7.2	(Bodzek and Dudziak, 2006)

Table 3   Summary of available data regarding trace organics removal by coagulation/flocculation

Category	Compound Class	Compound	Removal (%)	Coagulant Type	Coagulant Dose	pH	Reference
	Estrogen	Diethylstilbestrol	27	$Fe_2(SO4)_3$	12.2 mg/L	6.8-7.2	(Bodzek and Dudziak, 2006)
	Estrogen	Diethylstilbestrol	40	PACl	5.4 mg/L	6.8-7.2	(Bodzek and Dudziak, 2006)
	Progesterone	Progestogen	6	$Al_2(SO4)_3$	78 mg/L	6.8	(Westerhoff et al., 2005)
Pesticide	Herbicide	Metolachlor	28	$FeCl_3$	20-45mg/L	4.5-5.5	(Stackelberg et al., 2007)
	Herbicide	Clofibric acid	10	$FeCl_3$	40 mg/L	7.5	(Ternes, 2002)
	Insecticide	Diazinon	34	$FeCl_3$	20-45mg/L	4.5-5.5	(Stackelberg et al., 2007)
	Insecticide	Heptachlor	36	$Al_2(SO4)_3$	78 mg/L	6.8	(Westerhoff et al., 2005)
Pesticide	Insecticide	Aldrin	49	$Al_2(SO4)_3$	78 mg/L	6.8	(Westerhoff et al., 2005)
	Pesticide	a-Chlordane	24	$Al_2(SO4)_3$	78 mg/L	6.8	(Westerhoff et al., 2005)
Polycyclic Aromatic Hydrocarbon (PAH)		Chrysene	33	$Al_2(SO4)_3$	78 mg/L	6.8	(Westerhoff et al., 2005)
		Benzanthracene	26	$Al_2(SO4)_3$	78 mg/L	6.8	(Westerhoff et al., 2005)
Phthalate plasticizer		DEHP	53	$Al_2(SO4)_3$	50 mg/L	8.2-8.5	(Choi, 2006)
		DBP	49	$Al_2(SO4)_3$	50 mg/L	8.2-8.5	(Choi, 2006)
		DEP	46	$Al_2(SO4)_3$	50 mg/L	8.2-8.5	(Choi, 2006)

Table 4: Average removal efficiency according to trace organic compound class

Category	Compound Class	Average Removal (%)	Standard Deviation	N	Compounds showing over 50 % removal in this category	Reference
Pharmace-uticals	Analgesic/ Anti-inflammatory	35	23	15	Acetaminophen, diclofenac	(Boyd, 2003; Stackelberg et al., 2007; Suarez et al., 2009; Ternes, 2002; Vieno et al., 2006; Vieno, 2007; Westerhoff et al., 2005)
	Antibiotic	39	22	12	Minocycline-HCl, meclocycline-sulfosalicylate, CTC, democlocycline-HCl	(Choi et al., 2008; Stackelberg et al., 2007; Suarez et al., 2009; Vieno et al., 2006; Vieno, 2007; Westerhoff et al., 2005)
	Beta-blocker	34	25	9	Doxazosin, betaxolol	(Huerta-Fontela et al., 2011; Vieno, 2007)
	Cardiac	64	24	5	Clopidogrel, hydrochlorothiazide, warfarin	(Huerta-Fontela et al., 2011; Stackelberg et al., 2007)
	Psychiatric	32	39	14	Chlordiazepoxide, zolpidem, bromazepam	(Huerta-Fontela et al., 2011; Suarez et al., 2009; Ternes, 2002; Vieno et al., 2006; Vieno, 2007; Westerhoff et al., 2005)
	Stimulant	34	34	6	Amphetamine	(Bundy, 2007; Huerta-Fontela, 2008; Westerhoff et al., 2005)
	Pulmonary drug	6	7	3	--	(Huerta-Fontela et al., 2011)
	Hypolipidemic agent	26	15	2	--	(Ternes, 2002; Vieno et al., 2006)
Musk fragrance		**77**	**10**	9	Tonalide, galaxolide, celestolide	(Suarez et al., 2009)
Hormone		19	12	15	--	(Bodzek and Dudziak, 2006; Boyd, 2003; Westerhoff et al., 2005)
Pesticide		30	13	6	--	(Stackelberg et al., 2007; Ternes, 2002; Westerhoff et al., 2005)
Polycyclic Aromatic Hydrocarbon (PAH)		30	5	2	--	(Westerhoff et al., 2005)
Phthalate plasticizers		49	4	3	DEHP	(Choi, 2006)