Technical-economic comparison of chemical precipitation and ion exchange processes for the removal of phosphorous from wastewater

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Abstract

Chemical precipitation with the addition of ferric chloride is commonly used to remove phosphorous from wastewater. However, since its application involves also several disadvantages, studying alternative solutions is required. The present paper shows the results of a full-scale experimental work aimed at evaluating the efficiency of the ion exchange process using a polymeric anion exchange resins impregnated with aluminum ions in the removal of phosphorous from wastewater. The study compared the results obtained through this process with chemical precipitation, considering both technical and economic issues. At the same dosage of 6 L/h and influent concentration (about 6 mg/L), total removal efficiency of 95% and 78% (including also that occurring in the mechanical and biological processes) were achieved by means of the anion exchange process and chemical precipitation, respectively. However, in the latter case, this value was insufficient to ensure consistent compliance with the limit of 2 mg/L P_{tot} set on the effluent; to achieve this goal, ferric chloride dosage had to be risen up to 12 L/h, thus increasing the related costs. Furthermore, the anion exchange process generated a lower sludge production. Therefore, it showed to represent a valid alternative to chemical precipitation for P removal from wastewater.

Keywords: Chemical precipitation; Ion exchange; Phosphorous; Wastewater Treatment Plants

Introduction

Increase of nutrient content, such as nitrogen (N) and phosphorus (P), in water bodies through untreated discharges is the main responsible of the eutrophication process, that is a fast growth of algae and other forms of plants which produce adverse effects on the balance of organisms and water quality (Beccari et al., 1997; Jarvie et al., 2006). Therefore, it is mandatory to reduce nutrient load in the wastewater before its release into the receiving water body. In a Wastewater Treatment Plant (WWTP), P removal occurs through mechanical (e.g. in the primary sedimentation tank) and biological (due to bacterial synthesis) processes. However, these systems are usually unable to comply with the more stringent limits of P set on the effluent (EC, 1998). Then, an additional treatment unit specifically designed to enhance P removal, must be implemented and operated. To this purpose the mostly common process is the chemical precipitation through the addition of ferric chloride: in this way, orthophosphates react with iron to form iron-phosphate, that is slightly soluble and can be removed by sedimentation (Caravelli et al., 2010; Metcalf & Eddy, 2013). Although widely diffused, several are the drawbacks of this process: the presence of competing reactions between PO_4^{3-} and HCO_3^- can increase chemical requirements; pH value must be carefully controlled in order to optimize process efficiency; a significant production of chemical sludge is generated, which must be disposed of. Due to these issues, alternative solutions for reducing P content are strongly fostered (Nur et al., 2014; Acelas et al., 2015, Genz et al., 2004). Furthermore, due to the decreasing availability of natural resources worldwide, phosphorous recover from wastewater is receiving increasing attention for its reuse as in the fertilizer production (Sengupta and Pandit, 2011; Egle et al., 2015; IFDC, 2010).

Ion exchange process may represent a possible alternative system for enhancing P removal from wastewater (An et al., 2013; Blaney et al., 2007; Nur et al., 2014). It is a physical-chemical process, in which ionic species present on an exchanger (the resin) are being replaced by ionic species being initially in solution and having the same type of charge (Helfferich, 1995). The ion exchange resins are insoluble polymers containing highly basic or acidic functional groups, which are bound weakly to oppositely charged ions. In particular, for the removal of phosphorus from wastewater are used anionic resins that exploit the affinity between the orthophosphate and the polyvalent metals. The process can be highly efficient mainly depending on the type of resins and liquid solution composition; for instance, competitive ions can be present in the solution which possess a higher affinity towards the resin than the pollutant ions and consequently are preferably removed in the exchange process. Therefore, the resin must be properly selected; furthermore, pilot tests with the real solution and the resin are strongly recommended to find

53 out the best operating parameters and also to evaluate the removal efficiency that can be achieved under real

54 conditions.

55 The present study aimed at obtaining a technical and economic comparison between the anion exchange process

56 using a specifically designed resin, and the chemical precipitation with the addition of ferric chloride, for the

57 removal of P from a real wastewater. The experimental work was carried out at two full—scale Wastewater

58 Treatment Plants (WWTP1 and WWTP2, respectively), located in the central Italy, and managed by Acqualatina

59 S.p.A.. A polymeric anion exchange resin impregnated with aluminum ions was used in the study to accomplish

60 selective orthophosphate ions removal, exploiting the high affinity between these ions and polyvalent metals.

61 Comparison was carried out taking into account removal efficiency as well as sludge production and costs of

62 process operation.

63

64 **Methods**

65 *WWTP1 and WWTP2*

66 Both wastewater treatment plants treat a domestic sewage and have to respect the limit of 2 mg/L on total

67 phosphorous in the effluent, which is discharged into rivers. WWTP1 receives an average influent flow rate of 1200

68 m^3/d and includes the following main units: screening, degritting, biological reactors for denitrification-nitrification

69 and carbon removal (Pasveer system), secondary settlement, chlorination, sludge aerobic digestion, drying beds.

70 The anion exchange resin was applied in WWTP1 to the effluent of the aerobic biological tank prior to the

71 secondary sedimentation tank.

72 WWTP2 receives an influent flow rate of 6000 m^3/d as average. Lay-out of the water processing line consists

73 mainly of: degritting, primary sedimentation, denitrification-nitrification and carbon removal tanks, secondary

74 sedimentation and chlorination. Excess sludge is treated by thickening, aerobic digestion and centrifugation. Ferric

75 chloride was added in the pre-denitrification tank of WWTP2.

76 The plants receive approximately the same total P load, equal to 5 mg/L as average; however, the influent

77 composition is affected by a wide variability and phosphorous contents ranges between 2 and 13 mg/L. In the

78 absence of any additional treatment, both plants were unable to consistently respect the limit of 2 mg/L set on the

79 effluent by the law in force, also due to this wide variability.

80

81   *Chemicals*

82   The anion exchange resin (named CATFLOC 441), supplied by CATRA S.r.l., is made by insoluble organic polyamines

83   containing the functional group $Al(OH)_3$ and also Aluminum Polychloride (PAC) as coagulant. Three different

84   dosages of CATFLOC 441 were tested: 1 L/h, 3 L/h and 6 L/h, respectively. The resin operates through 2 steps: 1)

85   PAC allows destabilization of the surface charges, hydrolysis of the aluminum salts and formation of the functional

86   group $Al(OH)_3$; 2) polyamines act as aggregation nucleus for particles, thus improving sludge sedimentation.

87   Ferric chloride was added through an aqueous solution at 40% $FeCl_3$, dosed initially at a flow rate of 6 L/h and then

88   at 12.6 L/h.

89

90   *Analyses*

91   Removals at WWTP1 and WWTP2 were calculated based on P concentrations measured on samples collected from

92   the influent and the effluent over a 4 months experimental period.

93   The following parameters were also determined on these samples: total phosphorus (P_{tot}), dissolved phosphorus

94   ($P_{dissolved}$) and particulate phosphorus ($P_{particulate}$), COD, ammonia nitrogen (NH_3-N), nitrate nitrogen (NO_3-N), nitrous

95   nitrogen (NO_2-N) and total suspended solids (TSS). These parameters were determined by following standard

96   methods (APHA, 2005). Analytical determinations were carried out in duplicate on each sample and the average

97   was calculated. Furthermore, during the experimental study, the collected data on the influent and effluent from

98   the plants were statistically analyzed using logarithmic and normal distributions to find out the best one for the

99   representation; the average values reported in the manuscript have been obtained using this procedure.

100   Automatic devices were used for sampling. In the case of effluent, the sampling system consisted of 24-fixed

101   volume bottles, each one filled hourly per a total time interval of 24 h, in order to provide a composite sample. For

102   the influent, instantaneous sampling was used, applied prior to the pre-treatments in a section where the stream

103   was completely mixed in order to obtain a representative sample. The volume used for the analytical

104   determinations was always equal to 500 mL. These procedures were used for both plants. Samples were collected

105   every 4 days, as average, over the 4-months period of investigation, and stored at 4°C temperature before their

106   analysis.

107   The Imhoff cone tests were also conducted in order to determine the volume occupied by the sludge after 30

108   minutes. The results obtained were represented as (mL/g SS).
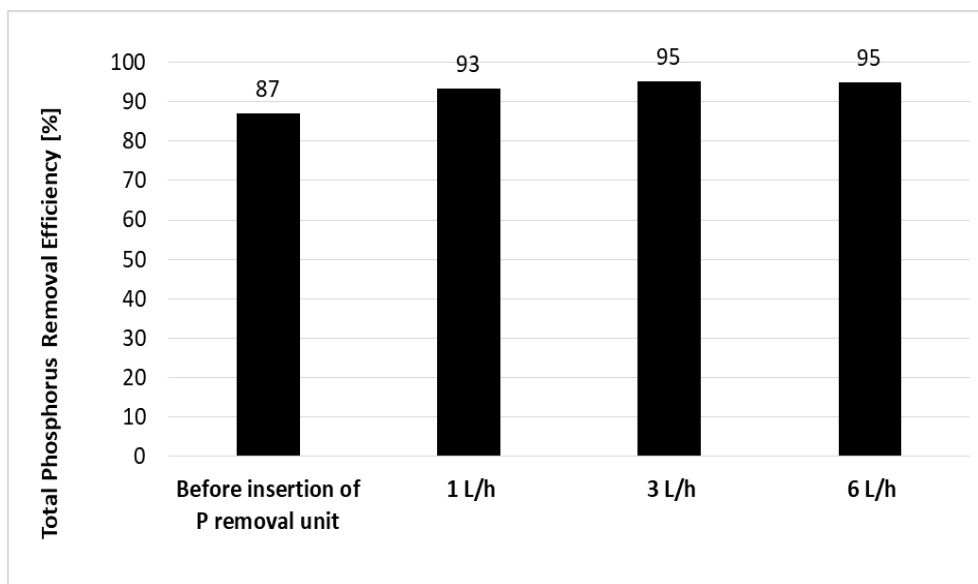
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Results and Discussion

Anion exchange process efficiency

Figure 1 shows the average removal of total P measured in WWTP1 prior to and after the anion exchange resin

dosage. The removal includes the effect of mechanical and biological treatments alone prior to the addition and

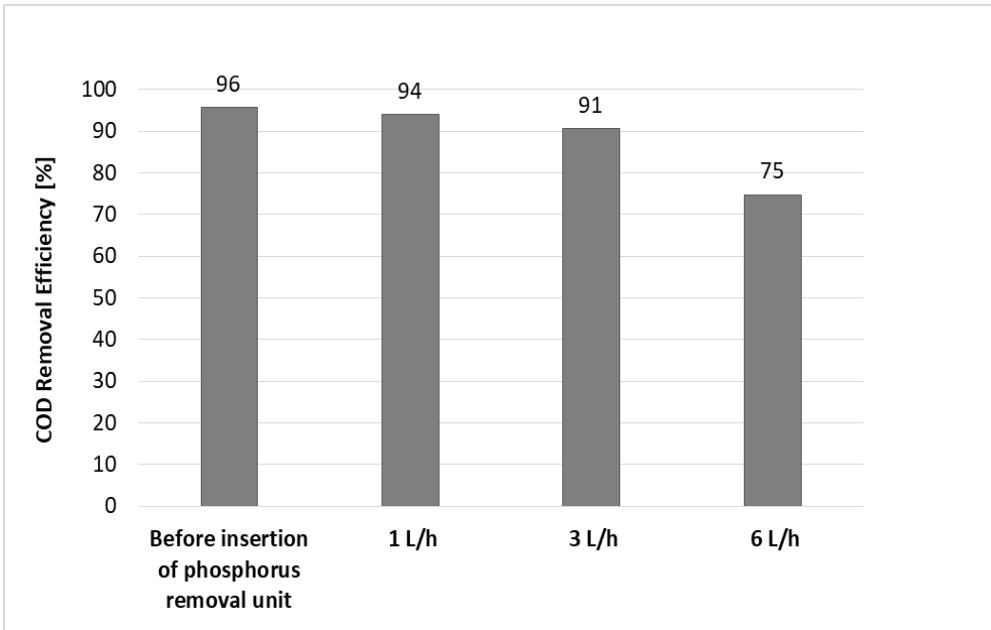then contribution of the ion exchange process also.

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116

Figure 1. Average removal efficiency of total P prior to and after the addition of the anion exchange process.

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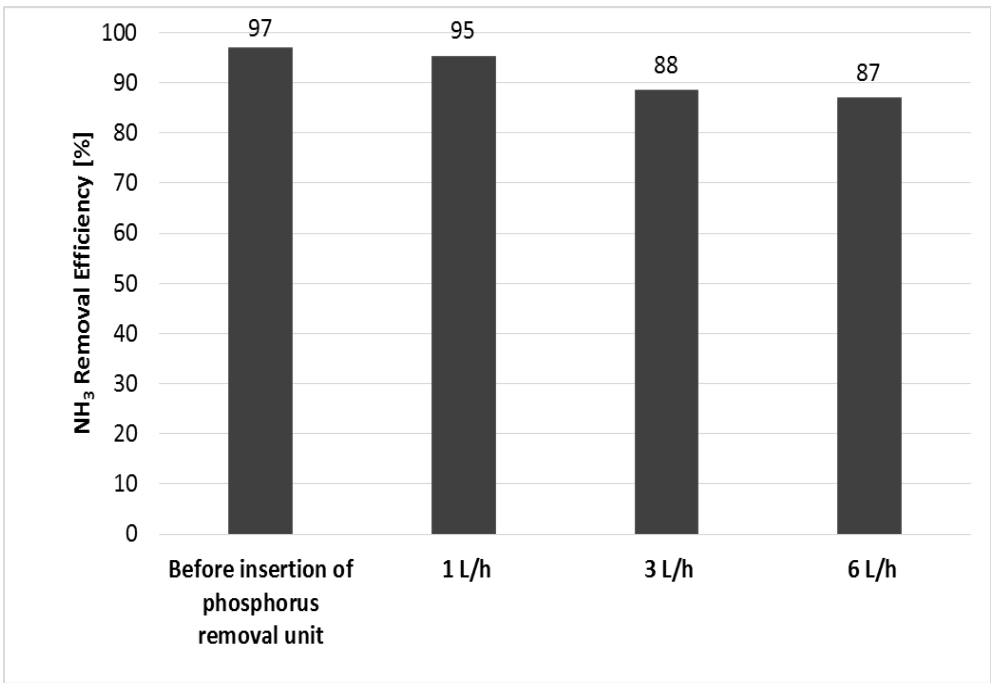
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Figure 2. Average COD removal efficiency prior to and after the addition of the anion exchange process.

Figure 3. Average NH_3 removal efficiency prior to and after the addition of the anion exchange process.

Based on the statistical analysis of the historical data of the influent and effluent phosphorus concentrations prior to the addition of the P removal process (average of 4.4 mg/L and 0.58 mg/L, respectively), it was calculated an average removal efficiency of 86.8%. Since the limit on the effluent is set at 2 mg/L total P, the WWTP1 was

129 capable of complying with the law in force. However, beside the limit on the effluent, the WWTPs have also

130 another constraint to observe, i.e. the maximum number of excesses allowed per year in the effluent with respect

131 to the limit. In the present case, such a number is equal to (2/12) x100 = 17%, whereas before the addition of the P

132 removal process it was equal to   20%. Therefore, it was calculated that the goal on the maximum number of

133 excesses could be respected only by increasing the efficiency up to 89.3%, which corresponded to an average P

134 concentration in the effluent of 0.47 mg/L, considering 4.4 mg/L as average influent P concentration.

135 Figure 1 highlights that the addition of the anion exchange process enhanced P removal with respect to the

136 previous period when it was due only to the mechanical and mainly biological (bacterial synthesis) processes;

137 besides, by increasing the dosage, the efficiency improved progressively rising from 93 to 95%. The beneficial

138 effect obtained was far beyond the initial goal set at 89.3%: this is likely to be attributed to the lower influent load

139 entering the plant during the experimental period. Therefore, the dosage might be reduced to save cost of the

140 chemical; more in general, due to the wide variability of the influent characteristics, an automatic dosing system

141 should be adopted, capable of adjusting the amount of resin to add based upon the required efficiency.

142 It is worth noting that during the experimental period, COD and ammonia nitrogen removal efficiency showed a

143 decrease with respect to the average values measured in the past, as shown in Figures 2 and 3, respectively, due to

144 lower influent concentrations; consequently, P removal due to only mechanical and biological processes lowered

145 from 86.8% to 70%. Therefore, the real incremental improvement of P removal due to CATFLOC 441 addition

146 accounted for a maximum of 25% (equal to the difference 95-70=25%).

147 Phosphorous time-profile in the influent during the experimental period provided average concentrations of total

148 and soluble fractions equal to 3.5 mg/L and 1.2 mg/L, respectively. These intervals are slightly lower than those

149 registered before the experimental period. About the effluent, total and dissolved phosphorous showed average

150 values of 0.21 mg/L and 0.09 mg/L, respectively.

151 About COD and ammonia nitrogen, as above mentioned, during the experimental period the influent values

152 showed average values of 195 mg/L and 23 mg/L, respectively, which are slightly below the historical data. The

153 effluent concentrations of COD, ammonia, nitrate and nitrite nitrogen remained close to those registered before

154 the addition of the resin and still far below the standards set by the law in force. Regarding TSS, the effluent

155 concentration showed a slight increase after the resin addition, but the standard of 35 mg/L TSS was still always

156 respected.

157   By exploring the effect on the different phosphorous fractions, it was observed that a decrease of TSS removal

158   efficiency in the secondary sedimentation determined a reduction of dissolved phosphorus removal: this likely

159   occurred because the higher presence of solids hindered the contact between the orthophosphate ions and the

160   ion exchange sites on the resin, thus reducing the efficiency of the process.

161   The Imhoff cone tests conducted with sludge samples collected by the WWTP1 showed that the resin addition

162   produced an improvement of sedimentation characteristics, as shown by Figure 4; in particular, the sludge volume

163   measured after 30 minutes settlement decreased from average of 187mL/g SS prior to the addition of CATFLOC

164   441 to about 126 mL/g SS and then to 116 mL/g SS as the dosage increased.

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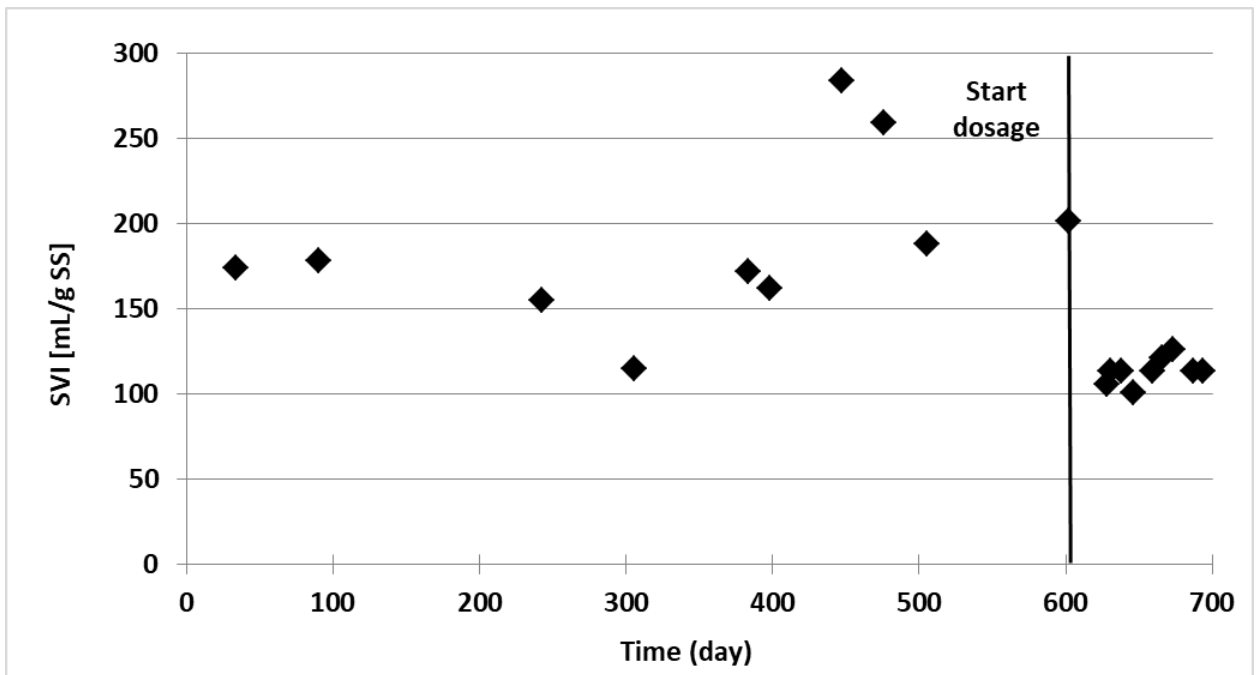
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167   **Figure 4**. Time-profile of SVI prior to and after the addition of the ion exchange process.

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169   About the effect on sludge production, an increase of about 25 kg/d was measured during the experimental

170   period, which represents an extra of about 13% with respect to the average value registered before. This

171   additional amount of sludge was calculated to be approximately equal to the resin weight applied during the

172   experimental work. It is worth noting that, based on the technical sheet data of the resin, the removal process is

173   carried out only through a transfer of ions between the bulk solution and the resin. Therefore, any extra sludge is

174   being produced beside that represented by the resin weight. These results suggest that for the future applications

175   of the resin to the WWTPs, the additional sludge production can be approximately predicted based upon the

176   amount added for the purpose.

177

178   *Chemical precipitation efficiency*

179   The average influent and effluent P concentrations in WWTP2 were statistically determined to be 6.2 mg/L and 1.4

180   mg/L, respectively, which provided an average removal efficiency of 77.7%. The maximum number of excesses

181   allowable with respect to the limit of 2 mg/L set on the effluent, is still (2/12)x100= 17%, which required the

182   concentration to be reduced to 0.72 mg/L. As a consequence, the removal efficiency should be risen up to 88% at

183   least.

184   Different dosages of ferric chloride solution were tested in WWTP2 with the aim to find out that one allowing to

185   consistently achieve this goal. When it was tested a dosage equal to that adopted for the resin in WWTP1, i.e. 6

186   L/h, it resulted in a total P removal efficiency of 78%, which was not enough. Therefore, the chemical dosage was

187   progressively increased up to the value of 12.6 L/h which was found to represent the lowest one allowing constant

188   compliance with the constraints posed on the plant effluent. Figure 5 shows the effect of this addition on P

189   removal. It can be observed that phosphorous content in the effluent became consistently lower than the limit.

190   Furthermore, this value also guarantees to maintain the required efficiency even against any change of the

191   phosphorous content in the influent, as frequently observed in the past.

192   About the main influent parameters monitored during the experimental period, total P, COD and ammonia-

193   nitrogen showed average values of 6.2 mg/L, 303 mg/L and 38 mg/L, respectively, which are slightly lower than the

194   historical data registered before; the effluent concentrations of COD, NH_3, NO_2 and NO_3 did not change

195   appreciably, remaining below the limits set by the law in force. About TSS, a slight increase was observed, but the

196   limit was still respected. Therefore, the presence of chemical precipitation in WWTP2 did not produce any

197   significant change on the removal of COD, NH_3, NO_2 and NO_3, as also observed in the case of WWTP1.

198   An increase of sludge production was registered in WWTP2 during the experimental period, likewise to WWTP1.

199   However, it was higher than in the previous case: indeed, at the optimal dosage of 12.6 L/h it accounted for about

200   105 kg/d, which corresponds to an extra of 17% with respect to the average historical data of plant operation. This

201   value was ascribed to chemical sludge production and therefore corresponding to the following stoichiometric

202   relationship:

203

$$Fe^{3+} + H_nPO_4^{3-n} \leftrightarrow FePO_4 + nH^+ \tag{1}$$

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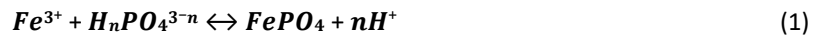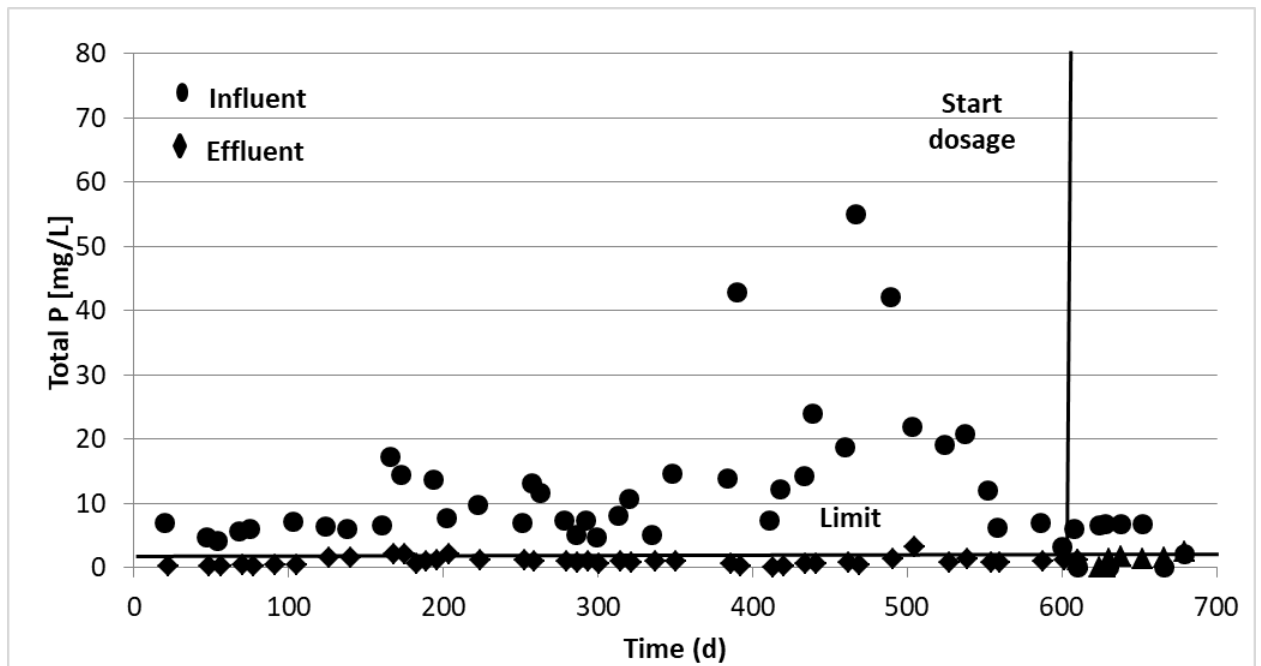
Figure 5. Effect of ferric chloride addition on total P removal in WWTP2.

208

209   *Operating cost evaluation*

210   The investigated WWTPs have similar lay-outs and received the same influent concentration of P on average basis.

211   The influent was likely to have the same composition since coming from a domestic sewage in both cases. Besides,

212   the plants had to respect the same limit set on the effluent for P and encountered difficulties in complying

213   consistently with it Therefore, due to these similarities, it is likely that a similar dosage of either resin or ferric

214   chloride would be required by both plants to achieve the same goal.

215   Comparison of operating costs of anion exchange and chemical precipitation processes was carried out considering

216   the following items: chemical purchase, energy consumption, sludge disposal. Personnel was not considered since

217   deemed comparable.

218   The unit cost of reagent purchase was significantly different: 0.75 €/kg and 0.19 €/kg, for the resin and ferric

219   chloride solution, respectively. However, due to the low dosage required for achieving the goal of removal, the

220   incidence of reagent cost in WWTP1 on the overall operating costs of the plant increased only of about 3%,

221   whereas in WWTP2 it did not change significantly. It is worth noting that treatment capacity of WWTP2 was much

222   higher than that of WWTP1. As a consequence, in WWTP2 the unit cost of reagent per treated flow rate was not

223   affected significantly and remained at approximately 11.5 €/m^3·d, whereas it increased from 6.2 €/m^3·d to 9

224   €/m^3·d in WWTP1. Energy consumption in both plants did not change significantly due to the addition of the

225   pumps used for chemical dosage. Cost of energy consumption per unit of flow rate remained higher in WWTP1

226   than in WWTP2 due to the different treatment capacity.

227   About sludge disposal costs, as mentioned above, implementation of the P removal processes determined an

228   additional sludge production in the plants. Due to the lower influent organic load registered during the

229   experimental period, sludge produced in the biological process and primary settlement (the latter in WWTP2 only)

230   decreased slightly. Therefore, the total amount of sludge did not change significantly as well as the disposal costs

231   which remained at about 30 €/m^3·d in WWTP2 versus 7 €/m^3·d in WWTP1. It has to be highlighted that a further

232   sludge addition impacts more in a plant such as WWTP2 where the cost for disposal is already high; besides,

233   chemical precipitation determined a greater sludge production than removal through the resin.

234   Figure 6 shows the percentage incidence of each cost item on the overall operating costs for the two systems,

235   calculated during the experimental period at the optimal dosage.

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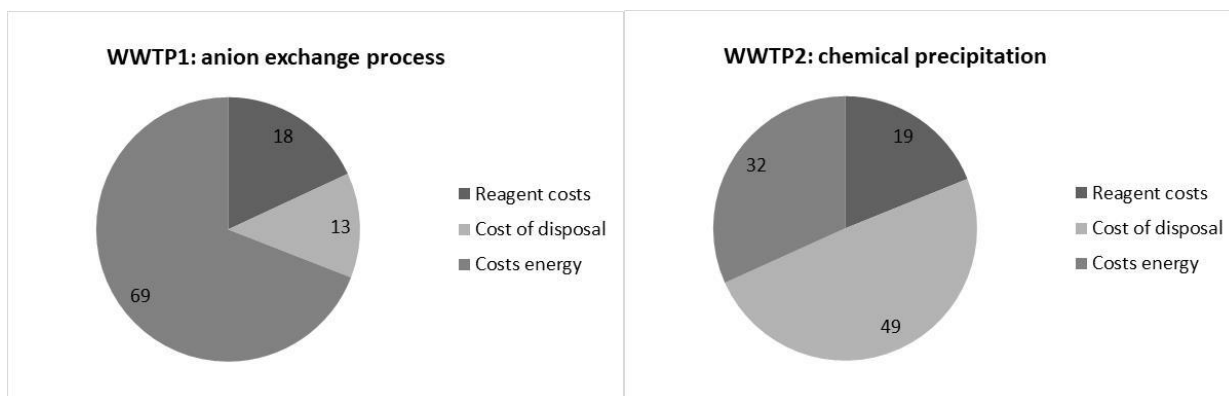
238   **Figure 6**. Incidence of cost items [%] for the two technologies of P removal on the overall operating costs.

239

240   **Conclusions**

241   The experimental study conducted at full-scale WWTPs showed that at the same dosage and influent P

242   concentration, the anion exchange process allowed to achieve the required removal efficiency, whereas chemical

243 precipitation in the other plant was unable to ensure consistent compliance with the limit set on the effluent; to

244 achieve this goal, a higher ferric chloride dosage had to be applied which implied increased costs.

245 Considering the additional sludge production, the anion exchange process determined a significantly lower

246 quantity with respect to chemical precipitation. Furthermore, the resin addition provided also the advantage of

247 the sludge settleability improvement.

248 These results show that excess phosphorus can be efficiently removed from wastewater by means of the anion

249 exchange resin tested in the present study. This process can be considered as a valid alternative from the technical

250 and economic points of view to the more diffused and well known chemical precipitation. Furthermore, the ion

251 exchange process offers also the opportunity to recover P from the exhausted resin.

252

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