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Title: Arsenic removal from water by coupling photocatalysis and complexation-ultrafiltration processes: a preliminary study

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Keywords: Water treatment; Arsenic removal; Complexation-ultrafiltration; Photocatalytic As(III) oxidation to As(V); As speciation.

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Abstract: Inorganic As removal from contaminated water has been studied by off-line coupling of photocatalysis and complexation-ultrafiltration (CP-UF), showing that this combination permits to obtain a quite complete arsenic removal from the treated water. Two commercial polymers, poly(dimethylamine-coepichlorohydrin-coethylenediamine) (PDEHED) and poly(diallyl dimethyl ammonium chloride) (PolyDADMAC) have been tested in the CP-UF process. The operating conditions (pH and polymer/As weight ratio) for As(V) complexation were determined finding values of 7.5/20 and 9.2/30 for PDEHED and polyDADMAC, respectively. The UF tests were performed by continuous diafiltration and diafiltration with volume reduction modes. The latter method permits to save the volume of washing solution during polymer regeneration. As(III) was not complexed, operating under the As(V) complexation conditions, thus a pre-oxidation step by using the photocatalytic approach was carried out to remove As(III) species. As(III) conversion to As(V) was evaluated by As speciation by using the CP-UF process for analytical purposes. Photocatalytic oxidation was successfully performed under UV radiation by using TiO<sub>2</sub> (0.05 mg L<sup>-1</sup>), O<sub>2</sub> and pH = 9. The oxidation was very fast during the first 10 minutes following a zero order kinetics ( $k = 0.83 \text{ mg L}^{-1} \text{ min}^{-1}$ ) and reaching 90% As(III) oxidation. A conceptual scheme coupling photocatalysis and CP-UF and some criteria to operate the CP-UF process useful to address it towards application are reported.

# **Arsenic removal from water by coupling photocatalysis and complexation-ultrafiltration processes: a preliminary study**

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## **Highlights**

Complexation-ultrafiltration and photocatalysis for As removal were offline coupled

pH and polymer/As ratio, giving 100% As(V) complexation, were determined

As speciation was performed by using the CP-UF process for analytical purposes

90% As(III) oxidation was obtained in 10 minutes under UV by using  $\text{TiO}_2$ ,  $\text{O}_2$  and pH 9

A scheme of online coupling and some criteria to run the CP-UF step are reported

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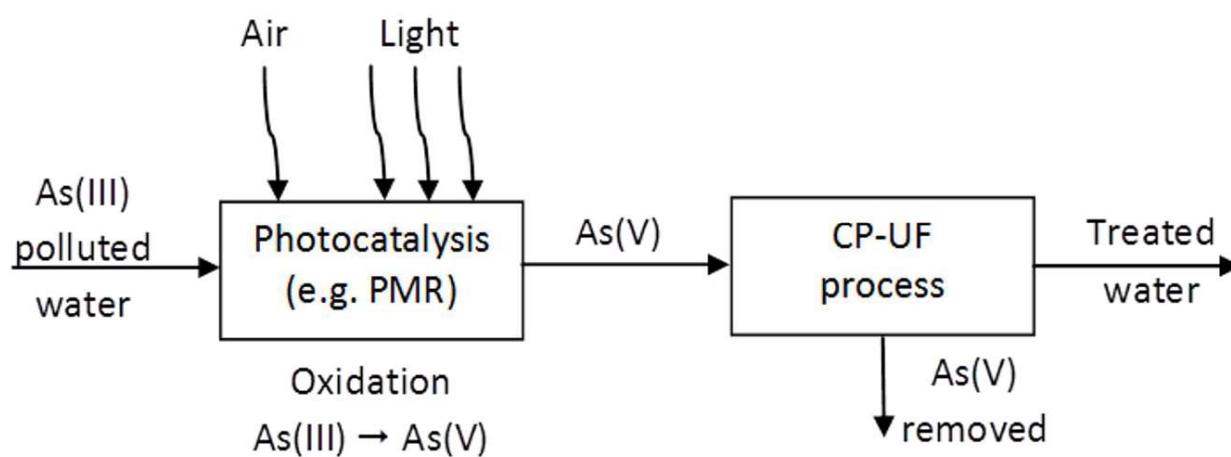
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### Graphical abstract



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## 34 **Abstract**

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37 arsenic removal from the treated water. Two commercial polymers, poly(dimethylamine-  
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49 some criteria to operate the CP-UF process useful to address it towards application are reported.

50

51 **Keywords:** Water treatment; Arsenic removal; Complexation-ultrafiltration; Photocatalytic As(III) oxidation  
52 to As(V); As speciation.

53

## 54 **1. Introduction**

55 The contamination of ground and surface water by arsenic is one of the major environmental problems in  
56 the present millennium, as many people are exposed to excessive arsenic amounts through contaminated  
57 drinking water (Kumar et al., 2016; Bhowmik et al., 2015; Suzuki et al., 2015). Acute and chronic exposure  
58 to arsenic via drinking water has been reported in many countries, especially Bangladesh, Argentina, Chile,  
59 India, Mexico, Mongolia, Thailand and Taiwan, where a large amount of groundwater is contaminated with  
60 arsenic at levels from 100 to 2000 ppb. In South Asia an estimated 140 million people drink arsenic  
61 contaminated water every day (Mukherjee et al., 2006; Ohno et al., (2007); Rahman et al., 2013; Singh and  
62 Vedwan, 2014; Singh et al., 2015).

63 Water contamination from arsenic is also a long-standing problem in Italy. Petrini et al. (2011), studying the  
64 natural arsenic contamination in waters from the Pesariis village in the Carnic Alps (North East of Italy)  
65 evidenced that ground and surface waters from that village are characterized by high As concentrations ( $\geq$   
66 900 ppb). Besides, the results of some sampling showed that the limit value for arsenic in 2014 is still not  
67 achieved in 37 water supply zones in Latium Region (Cubadda et al., 2015).

68 The high levels of As in ground and surface water in the various countries are predominantly of geogenic  
69 origin (Li et al., 2015; Sharma et al., 2014). Anthropogenic sources of As include various industrial activities,  
70 pesticides, herbicides, and fertilizers.

71 Arsenic occurs in natural water in several chemical forms and oxidation states, prevalently in the trivalent  
72 (As (III), arsenite ion) and pentavalent (As (V), arsenate ion) forms. The trivalent form is the most dangerous  
73 owing to its higher toxicity and mobility (Cullen and Reimer, 1989; Jain and Ali, 2000). It is present in highly  
74 reducing environments such as those of the aquifer (Park et al. 2016).

75 In 2001 the World Health Organization (WHO) and US Environmental Protection Agency (US-EPA) set the  
76 new Maximum Contaminant Level (MCL) standard for arsenic in drinking water to  $10 \mu\text{g L}^{-1}$  (US-EPA, 2001;  
77 Li et al., 2016). So it is essential to develop economical and effective methods for arsenic removal from  
78 drinking water.

79 Conventional technologies for arsenic removal include adsorption and coagulation/precipitation (Lata and  
80 Samadder, 2016; Nicomel et al., 2015; Beduk, 2016). Adsorption processes are limited by the low selectivity  
81 of the process, the difficulties of particle handling and the production of a spent regenerating media which  
82 contains many contaminants thus requiring an appropriate disposal (Barakat, 2011). Disadvantages of  
83 coagulation/precipitation process are: i) production of big amounts of sludge containing residues of the  
84 reagent(s) used, ii) possible presence of residual reagents in treated water and iii) low process selectivity.

85 These technologies result efficient in treating water containing As(V), but they are inefficient for the  
86 removal of As(III). This behaviour can be explained considering the three pKa of  $\text{H}_3\text{AsO}_4$  ( $\text{pKa}_1 = 2.22$ ,  $\text{pKa}_2 =$   
87  $6.98$  and  $\text{pKa}_3 = 11.53$ ) and of  $\text{H}_3\text{AsO}_3$  ( $\text{pKa}_1 = 9.2$ ,  $\text{pKa}_2 = 12.1$  and  $\text{pKa}_3 = 12.7$ ), which are inorganic forms of  
88 As(V) and As(III), respectively. At neutral pHs the As(V) is completely in ionic form ( $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ ),  
89 while As(III) is in molecular form. In particular, at pH below 9.2 the arsenite is uncharged, thus unable to  
90 interact with adsorbing/coagulating agents. Thus, As(III) oxidation into the more easily extractable As(V)  
91 form is the first step to an efficient As removal process (Rivas et al., 2011a; Zhang et al., 2016).

92 The oxidation procedure is mainly performed by the addition of chemical reagents such as  $\text{O}_2$  and/or ozone  
93 (Kim and Nriagu, 2000; Pettine et al., 1999), hydrogen peroxide (Du et al., 2014; Kim et al., 2015),  
94 manganese dioxide (Driehaus et al, 1995), potassium permanganate, chlorine, sodium hypochlorite and  
95 chlorine dioxide (Ghurye et al., 2004). Although these reagents are effective in oxidizing trivalent arsenic,  
96 they may cause several secondary problems owing to the formation of by-products or the presence of  
97 residuals.

98 Photocatalysis (PC) is an Advanced Oxidation Process extensively studied in literature (Molinari et al.,  
99 2008a; Bethi et al., 2016; Lelario et al., 2016), which represents an interesting alternative for oxidizing  
100 As(III) to As(V). Some advantages of PC are: i) use of safe photocatalysts (mainly  $\text{TiO}_2$ ), ii) use of mild  
101 oxidants, iii) operation under mild conditions, iv) no production of harmful chemicals, v) good alternative to  
102 the energy-intensive conventional treatment methods and vi) possibility of combination with other physical

103 and chemical technologies (e.g. membrane separations) (Ganiyu et al., 2015; Molinari et al., 2015). Yao et  
104 al. (2012) demonstrated that PC can rapidly oxidize arsenite to arsenate, since the redox potential of the  
105 As(V)/As(III) couple is lower than the valence band potential. So the photo-generated holes have enough  
106 thermodynamic potential to oxidize As(III) to As(V).

107 Once As(III) is converted to As(V), it is important to find effective methods for its removal from water,  
108 achieving the legislation limits and avoiding the disadvantages of traditional separation processes.

109 In our previous works the complexation-ultrafiltration (CP-UF) was studied to achieve an efficient  
110 separation and/or recovery of some metallic ions from aqueous solutions (Molinari et al., 2004, 2007,  
111 2008b). The key point of the CP-UF technique is the binding of the metallic ions to be separated to a  
112 macromolecular water soluble species (Trivunac and Stevanovic, 2006). This complexation step is then  
113 followed by an UF step, where the polymer and its metal-complexes are retained by the membrane, while  
114 the uncomplexed species permeate through the membrane.

115 Recovery of the polymer is a key step in terms of process sustainability, which is achieved by releasing the  
116 metal from the polymer-metal complex, e.g., by decreasing the pH of the solution and subsequent UF.

117 In a series of works the Rivas group (Rivas et al. 2006, 2010; Palencia et al., 2009) studied the application of  
118 CP-UF in the separation of arsenic ions from water, evidencing the influence of the operating pH and of the  
119 polymer/As molar ratio on arsenate retention.

120 The same group (Rivas et al., 2009, 2011b) also studied the possibility to couple the electro-catalytic  
121 oxidation of As(III) to As(V) followed by CP-UF for As(V) removal obtaining a complete arsenic removal from  
122 the treated water.

123 Starting from the described approach, the basic idea of the present preliminary work consists in using the  
124 photocatalytic oxidation of As(III) to As(V) and then the CP-UF process giving particular attention to some  
125 aspects that can be successively used to draw a real process to remove As(V) from aqueous media. The  
126 photocatalytic process, compared to the electro-catalytic process, presents the potential advantage of  
127 using, in perspective, energy from solar light as oxidizing power, resulting in a more green process. Some  
128 CP-UF tests using two water soluble polymers have been carried out for determining the optimal chemical  
129 conditions (pH and polymer/metal weight ratio) for As(V) removal from water. These tests have been also  
130 used as analytical tool for determining As(III) and As(V) concentration in the photocatalytic tests. Two  
131 diafiltration mode (continuous and with volume reduction) were tested to study As(V) complexation giving  
132 also some criteria for utilizing them on application scale. The photocatalytic oxidation of As(III) to As(V) in  
133 the presence of TiO<sub>2</sub> as the catalyst and O<sub>2</sub> as the oxidant has been studied and a conceptual scheme to  
134 couple the two process is reported.

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138 **2. Materials and Methods**

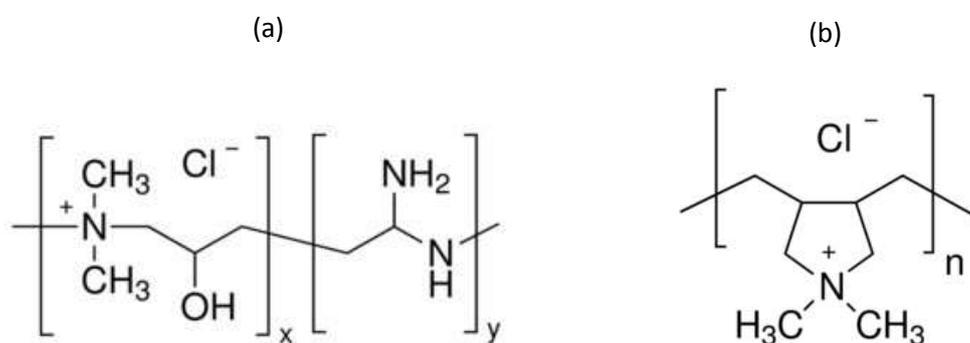
139 **2.1. Reagents**

140 Sodium meta arsenite  $\text{NaAsO}_2$  (MW = 129.91  $\text{g mol}^{-1}$ , purity  $\geq 98\%$ ) and di-sodium hydrogen arsenate  
141 hepta-hydrate  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (MW = 312.01, purity  $\geq 98\%$ ) from Sigma Aldrich were used as arsenite and  
142 arsenate source, respectively.

143 Poly(dimethylamine-coepichlorohydrin-coethylenediamine) (PDEHED, 50 % wt. solution in water, average  
144 MW = 75,000  $\text{g mol}^{-1}$ ) and poly(diallyl dimethyl ammonium chloride) (polyDADMAC, 20% wt. solution in  
145 water, average MW = 100,000-200,000  $\text{g mol}^{-1}$ ) (Fig. 1) from Sigma Aldrich were tested as the water soluble  
146 complexing polymeric agents.

147

148



150 **Fig. 1.** Structural formulas of the complexing polymeric agents tested: (a) PDEHED and (b) polyDADMAC.

151 Titanium dioxide ( $\text{TiO}_2$ ) P25 type from Evonic-Degussa (specific surface area = 44  $\text{m}^2 \text{g}^{-1}$ , crystallographic  
152 phase ca. 80% anatase and 20% rutile, band gap 3.2 eV) was used as photocatalyst.

153 Ultrapure water from Milli-Q (Millipore) was used to prepare the aqueous solutions and during membrane  
154 characterization.

155 Sodium hydroxide pellets (NaOH, 97% purity) from Aldrich and hydrochloric acid (HCl, 37% w/w) from Carlo  
156 Erba Reagenti were used to prepare the aqueous solutions for adjusting the pH of the aqueous solution.

157 Nitric acid ( $\text{HNO}_3$ , 65% wt. solution in water) from Carlo Erba Reagenti was used to prepare the sample for  
158 ICP-MS analyses.

159 Ultrapure water, obtained from Milli-Q equipment by Millipore, was used to prepare the aqueous phases  
160 used during all the UF or photocatalytic tests.

161

162 **2.2. Analytical and Instrumentation**

163 Arsenic concentrations were determined by using two analytical kits named Merkoquant from Merk (see  
164 supporting information).

165 Some arsenic concentrations were also measured by using an ICP-OES (Optima 2100 DV, Perkin Elmer),  
166 finding a good agreement with Merkoquant kits. The comparison of the results obtained with these two

167 methods showed a little difference (within 5%) caused by interferences of the kits, probably for the  
168 presence of the polymer in the samples.

169 A pH meter (WTW Inolab Terminal Level 3) with a glass pH-electrode SenTix 81 (WTW), was used for pH  
170 measurements.

171 Total organic carbon (TOC) measurements were performed by using a TOC-VCSN from Shimadzu.

172

### 173 2.3. Apparatus and methods

174 Diafiltration tests were carried out in an experimental set-up with a maximum chamber capacity of 72 mL  
175 and an exposed membrane surface area of 14.5 cm<sup>2</sup> described in our previous works (Molinari et al., 2007)  
176 and briefly described in supporting information.

177 A flat sheet UF membrane of the Iris series, made of polyethersulphone (PES) and manufactured by Tech-  
178 Sep, with molecular weight cut-off 30 kDa, named Iris 30, was used in all experiments measuring rejection  
179 and permeate flux.

180 Photocatalytic tests were carried out in the experimental set-up (Fig. S1) as reported in supporting  
181 information.

182 Adsorption tests were carried out for evaluating the adsorption of As(III) and As(V) at acidic and alkaline  
183 pHs on TiO<sub>2</sub> photocatalyst, as described in supporting information.

184 The diafiltration tests were carried out by using the two diafiltration modes:

- 185 - continuous (DF-c) by continuously feeding to the permeation cell an aqueous solution at the same  
186 pH of the feed phase (70 mL) previously loaded into the cell. One diafiltration volume (DV) is  
187 obtained when a permeate volume, equal to the initial, is collected (70 mL);
- 188 - with volume reduction (DF-vr) by permeating half (35 mL) of the solution loaded into the cell. One  
189 DV corresponds to half of the initial (35 mL). If the process should be continued the initial volume  
190 should be restored with the solution at the same feed pH and then continuing the steps of volume  
191 reduction and solution addition obtaining consecutive DV of permeate.

192 In the present work, because we were interested only to As complexation with the polymer we stopped the  
193 diafiltration to the first DV and then applied a mass balance to estimate the complexation percentage (C%)  
194 applying the following equation:

$$195 \quad C\% = \frac{m_{As,in} - (m_{As,1DV} + m_{As,Ret})}{m_{As,in}} \times 100 \quad (1)$$

196 where  $m_{As,in}$  is the mass of arsenic initially contained in the feed,  $m_{As,1DV}$  is the mass of arsenic contained in  
197 the first DV and  $m_{As,Ret}$  is the mass of non complexed arsenic remained in the solution in the retentate.

198 Considering the MWCO, the membrane should be 100% permeable to As(V), so the mass of As(V) into the  
199 retentate can be obtained applying the theory of diafiltration. In particular, for a 100% permeable solute  
200 (0% retention) a determinate percentage of solute is present in the 1<sup>st</sup> DV (%<sub>s<sub>p</sub></sub>), while the remaining  
201 fraction (%<sub>s<sub>r</sub></sub>) stays into the retentate. So, the term  $m_{As,Ret}$  can be calculated as follows:

202 
$$m_{As,Ret} = \frac{m_{As,1DV}}{\%s_p} \times \%s_r \quad (2)$$

203 In the continuous diafiltration  $\%s_p = 0.63$  and  $\%s_r = 0.37$  while in the volume reduction mode  $\%s_p = \%s_r =$   
 204  $0.50$  (Schwartz, 2003; Beaton and Klinkowski, 1983).

205 The rejection of the polymer was determined by the TOC values from the following equation:

206 
$$R\%(TOC) = (1 - (TOC_p / TOC_r)) \times 100 \quad (3)$$

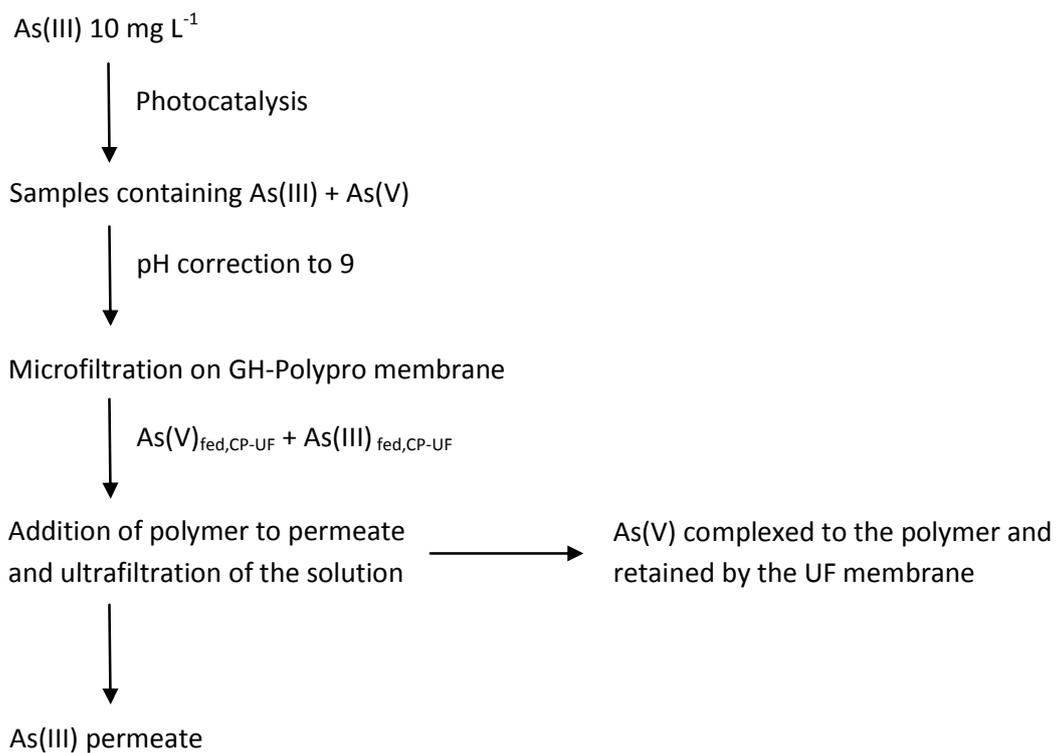
207 where  $TOC_p$  represents the average total organic carbon concentration in the two permeates and  $TOC_r$  is  
 208 the TOC concentration of the retentate.

209 In the photocatalytic tests, As(III) conversion to As(V) was calculated as follows:

210 
$$\text{Conversion (\%)} = (([As(III)]_{in} - [As(III)]_{photo}) / ([As(III)]_{in})) * 100 \quad (4)$$

211 where  $[As(III)]_{in} = 10 \text{ mg L}^{-1}$  is the initial As(III) concentration in the solution submitted to photocatalysis,  
 212 and  $[As(III)]_{photo}$  is As(III) concentration in the photocatalytic step at a certain time. The  $[As(III)]_{photo}$  was  
 213 determined by discriminating between As(III) and As(V) by applying the CP-UF process as an analytical tool  
 214 according to Scheme 1 which will be explained later in par. 3.3.3.

215



216

217 **Scheme 1.** Methodology for As(III) and As(V) speciation in the solution submitted to photocatalytic tests.

218

### 219 3. Results and Discussion

#### 220 3.1. Determination of optimal chemical conditions for As(V) complexation

221 Considering that the objective of applying the CP-UF process in the treatment of As contaminated water is  
 222 to obtain a permeate quality within the legislation limit, i.e. As concentration lower than  $10 \mu\text{g L}^{-1}$ , a first

223 step of this study consisted in the determination of the optimal chemical conditions (pH and polymer/metal  
224 weight ratio) for obtaining the total complexation of arsenate ions by using the PDEHED and PolyDADMAC  
225 polymers. Polymer regeneration is also fundamental in view of economical feasibility of the process, so the  
226 chemical conditions for As(V) release by the polymer were also determined.

227 Complexation conditions were determined by submitting the solutions to diafiltration tests changing each  
228 time the pH of the aqueous feed phase.

229 For calculating C% (see eq. (1)) the determination of the concentration of uncomplexed As(V) is needed.

230 This is done by separating the As(V) free in solution from that one bound to the polymer by using the two diafiltration  
231 modes previously described.

232

### 233 *3.1.1. Tests performed in continuous diafiltration*

234 These tests were carried out at 4 bar by using the PDEHED polymer as complexing agent. Two permeate  
235 volumes of 35 mL were collected but the calculation was referred to a total permeate volume equal to the  
236 feed one.

237 The concentration of As, TOC, pH and filtration time were measured for each 35 mL of permeate. The first  
238 set of tests was carried out for determining the complexation and de-complexation pHs. These tests were  
239 carried out at fixed arsenic and polymer concentrations ( $10 \text{ mg L}^{-1}$  and  $200 \text{ mg L}^{-1}$ , respectively)  
240 corresponding to a polymer/metal weight ratio of 20 and changing the operating pH. Obtained results,  
241 summarized in Fig. 2 in terms of arsenic complexation versus the pH, show practically a complete As  
242 complexation in the pH range 6 – 7.5. In particular the average As concentrations in the permeates ( $[\text{As}]_{p,av}$ )  
243 were  $0.0$  and  $7.0 \mu\text{g L}^{-1}$  for pH 7.5 and 6, respectively. Thus, the optimal pH for As(V) complexation by the  
244 polymer PDEHED is in that range. The decrease of complexation observed at pH 10.2 was probably caused  
245 by the competition of  $\text{OH}^-$  ions with the arsenate anions. As(V) complexation significantly decreased by  
246 decreasing the operating pH at acidic values ( $< 4.2$ ), giving an unacceptable average concentration in the  
247 permeate ( $[\text{As}]_{p,av} = 1.584 \text{ mg L}^{-1}$ ). The negligible As(V) complexation obtained at pH = 2, indicates this as the  
248 de-complexation pH.

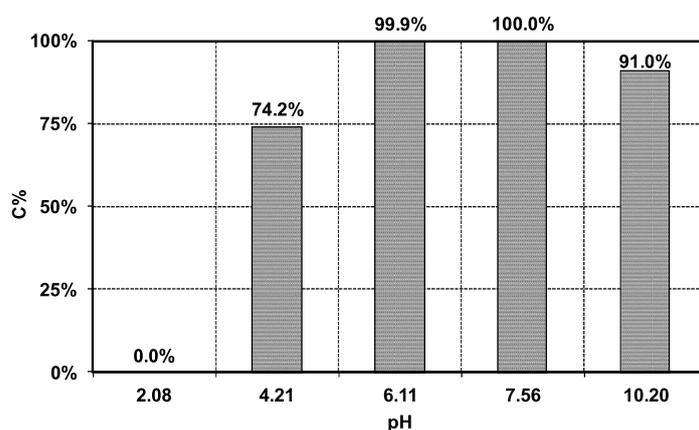
249 The trend of As(V) complexation vs. the operating pH can be explained by considering both arsenic(V)  
250 speciation (Fig. 3) and the interaction mechanism between the polymer and the arsenate ion which is of  
251 ionic exchange type. At pH 6-7.5 As(V) is in ionic form ( $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ ) and PDEHED tends to release  
252 its chlorine ion  $\text{Cl}^-$  exchanging it with the As(V) ions contained into the aqueous matrix (see eqs. (5) and (6))  
253 thanks also to the higher charge of the  $\text{HAsO}_4^{2-}$  ion. At lower pH (4.2) As(V) is all in ionic form as  
254 monovalent ion  $\text{H}_2\text{AsO}_4^-$ , and the tendency of PDEHED of releasing its chlorine ion  $\text{Cl}^-$  is lower because of  
255 the higher  $\text{Cl}^-$  concentration in the aqueous media (HCl is used to acidify the solution), so the ion exchange  
256 reaction is less favoured. These results are in agreement with Rivas et al. (2006). They observed that, in

257 general, As(V) is more easily retained at pHs between 6 and 9 in comparison with lower pHs, since the  
 258 anionic exchanger (as PDEHED) prefer divalent anions with respect to monovalent anions.

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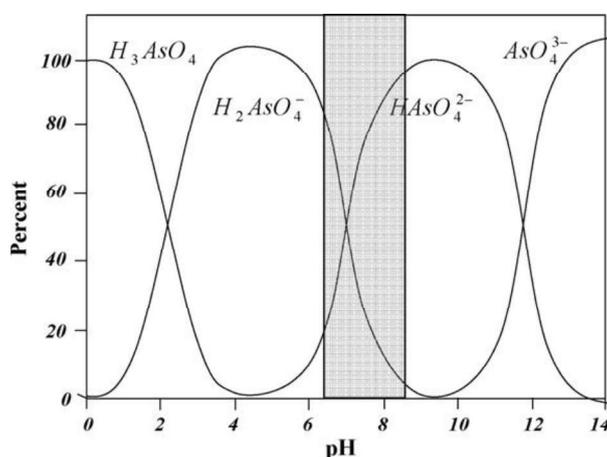


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264 **Fig. 2.** Arsenic(V) complexation vs. pH in DF-c mode tests at polymer/arsenic weight ratio = 20 ([PDEHED] =  
 265 200 mg L<sup>-1</sup>; [As(V)] = 10 mg L<sup>-1</sup>; TMP = 400 kPa, T = 25 ± 1 °C).

266

267



268

269 **Fig. 3.** Arsenic(V) speciation as function of solution pH (Guan et al., 2012).

270

271 TOC rejections evidenced an average value of 95.8 ± 0.8 showing that approximately 4% of the polymer  
 272 permeated across the membrane in the pH range 2-10. This trend is caused by the poly-disperse nature of  
 273 the commercial polymer and it can be solved by pre-filtrating the polymer, removing the smaller polymer  
 274 chains, like it was reported in our previous works (Molinari et al, 2004, 2007, 2008b).

275 Considering the concentration of As(V) into the two collected (35 mL volume) permeates at the different  
 276 pHs, the average concentration found in 1 DV (70 mL) can be calculated and then from a mass balance the

277 percentage of arsenic (%As<sub>,1DV</sub>) over the initial can be calculated and reported in Table 1. From the theory  
 278 of diafiltration in continuous mode it is known that for a 100% permeable solute (0% retention) the  
 279 percentage of solute present in the 1<sup>st</sup> DV is 63% (Schwartz, 2003; Beaton and Klinkowski, 1983). So the  
 280 value of 60% at pH 2.08 in Table 1 confirms that As(V) is not complexed at this pH and has a retention close  
 281 to zero.

282

283 **Table 1:** As(V) concentration in the permeates vs. pH in DF-c mode tests at polymer/arsenic weight ratio =  
 284 20 ([PDEHED] = 200 mg L<sup>-1</sup>; [As(V)] = 10 mg L<sup>-1</sup>; TMP = 400 kPa, T = 25 ± 1 °C).

pH	[As] <sub>p1</sub>	[As] <sub>p2</sub>	%As <sub>,1DV</sub>
			(w/w)
	mg L <sup>-1</sup>	mg L <sup>-1</sup>	
2.08	6.50	5.50	60.0
4.21	1.80	1.37	15.8
6.11	0.014	0.00	0.1
7.56	0.00	0.00	0.0
10.20	0.74	0.47	6.0

285

286 Once determined the optimal pH for As(V) complexation/removal by using the PDEHED polymer, some DF-c  
 287 mode tests were carried out in order to determine the optimal polymer/As weight ratio where a C% close  
 288 to 100% is obtained. These tests were carried out at fixed pH (6 and 7.5, which are optimal values) and  
 289 changing the polymer/As ratio. Considering the satisfactory results obtained by operating at 20 weight ratio  
 290 in terms of As complexation (see Fig. 2), and that a decrease of polymer concentration could result in a  
 291 reduction of membrane fouling, lower polymer amounts corresponding to 15, 10 and 5 weight ratios were  
 292 tested. Membrane rejections and membrane fouling were determined. This last parameter was quantified  
 293 by using the J/J<sub>w</sub> parameter, where J is the permeate flux measured during the diafiltration and J<sub>w</sub>  
 294 represents the pure water flux of the membrane.

295 Obtained results are summarized in Table 2. pH 7.5 and the polymer/As weight ratio of 20 were the optimal  
 296 chemical conditions that maximize As complexation obtaining an As free permeate (a not detectable As  
 297 concentration was obtained by using ICP-OES instead of the analytical kit in this case). Satisfactory results  
 298 were also obtained by operating at pH 6 and polymer/As ratios 20 and 15, obtaining a permeate  
 299 concentration within the legislation limit of 10 µg L<sup>-1</sup>. Despite the acceptable water quality and the lowest  
 300 membrane fouling observed at pH 6, pH 7.5 is preferable since wastewater containing As possess a pH in  
 301 the range 7-8. Thus the operation at pH 7.5 requires lower pH corrections, with respect to pH 6, which  
 302 means lower consumption of chemical reagents. pH 7.5 and polymer/As weight ratio 15 can be used when  
 303 the complete As removal is not required, but the permeate is within the legislation limit.

304

305 **Table 2:** Results of the tests in DF-C mode at two pH values by changing the polymer/arsenic weight ratio  
 306 ([PDEHED] = 50/100/150/200 mg L<sup>-1</sup>; [As(V)] = 10 mg L<sup>-1</sup>; TMP = 400 kPa, T = 25 ± 1 °C).

		Polymer/As weight ratio			
		5	10	15	20
[As] <sub>1DV</sub> (μg L <sup>-1</sup> )	pH 6	786	50	7	7
	pH 7.5	800	88	7	0
C% (As(V))	pH 6	88.0	99.2	99.9	99.9
	pH 7.5	86.6	98.7	99.9	100.0
R% TOC	pH 6	89.7	96.9	97.4	95.8
	pH 7.5	88.2	92.7	95.5	96.3
J/J <sub>w</sub>	pH 6	0.79	0.66	0.61	0.58
	pH 7.5	0.61	0.53	0.48	0.46

307

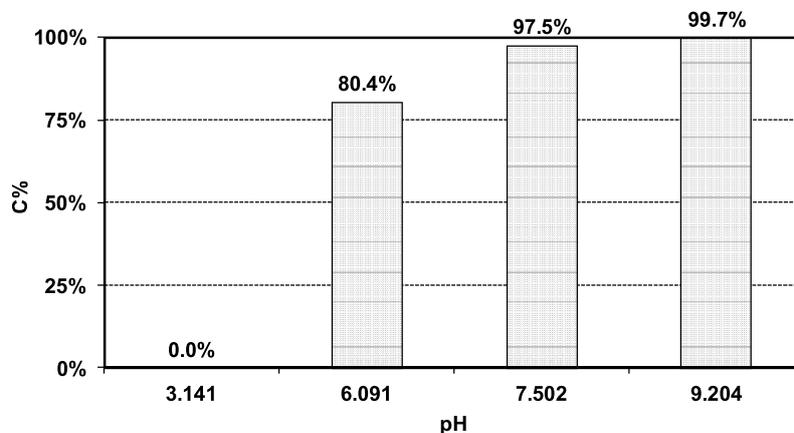
### 308 3.1.2. Tests performed in diafiltration with volume reduction (DF\_vr) mode

309 These tests were carried out at 2 bar by using the PolyDADMAC polymer as complexing agent for  
 310 determining the operating conditions (pH and polymer/As ratio) to obtain an acceptable permeate quality.  
 311 This method can be alternative to that described in the previous paragraph and it can be faster as it will be  
 312 explained later. This type of tests were also carried out by using the PDEHED polymer in the optimal  
 313 conditions (pH 7.5 and polymer/As ratio 20) for comparing the two techniques and the performance of  
 314 both polymers under the same operating mode. These tests were performed by permeating 35 mL of  
 315 solution, leaving 35 mL as residual volume of retentate. Preliminary tests showed that the permeation of 35  
 316 mL did not significantly influence system performance (i.e. C%, R(TOC) and J), and that the performance  
 317 and the information obtained operating with volume reduction were similar to that one obtained in  
 318 continuous mode, with the advantage of simpler and faster operation. As concentration, TOC, pH and J  
 319 were measured while C%, and R%(TOC) were calculated by eqs. (1) and (3).

320 The first set of tests with the polyDADMAC polymer were carried out at fixed As and polymer  
 321 concentrations (10 mg L<sup>-1</sup> and 200 mg L<sup>-1</sup>, respectively) corresponding to a polymer/metal weight ratio of 20  
 322 and changing the operating pH, to determine the complexation and de-complexation pHs. The results,  
 323 summarized in Fig. 4, show that the highest As complexation (99.7%) was obtained at pH 9.2. An  
 324 unacceptable As concentration in the permeate of 30 μg L<sup>-1</sup>, three times higher than WHO limit, was  
 325 obtained at this pH. The negligible As(V) complexation obtained at pH = 3.14, indicates this as the de-  
 326 complexation pH for this polymer.

327 The trend of As complexation vs. the pH can be explained by using the same consideration previously  
328 reported in the case of the PDEHED polymer, since also polyDADMAC complexes As(V) anions by an ionic  
329 exchange mechanism.

330



331

332 **Fig. 4.** Arsenic(V) complexation vs. pH in the DF-vr tests at polymer/arsenic weight ratio = 20  
333 ([polyDADMAC] = 200 mg L<sup>-1</sup>; [As(V)] = 10 mg L<sup>-1</sup>; TMP = 200 kPa, T = 25 ± 1 °C).

334

335 TOC rejections higher than 98% were obtained regardless of the operating pH and the complexation  
336 degree. This result, better than that obtained by using the PDEHED polymer in the operating DF-c mode,  
337 can be explained by considering the higher average molecular weight of PolyDADMAC (100-200 kDa)  
338 compared to PDEHED (75 kDa).

339 Considering that at pH = 9.2 the polymer gave the highest As(V) complexation with a polymer/As weight  
340 ratio of 20 (see Fig. 4) which, however, was not satisfactory (As concentration in the permeate 30 µg L<sup>-1</sup>),  
341 other DF-vr tests were carried out at this pH by increasing this ratio. It was fixed to 30 and 40,  
342 corresponding to PolyDADMAC concentration of 300 and 400 mg L<sup>-1</sup>. The results, summarized in Table 3,  
343 evidenced lower As concentration in the permeate and then an higher As complexation (99.9%) by  
344 operating with a polymer/As ratio of 30. A further increase of this ratio did not result in an increase of As  
345 rejection, but resulted in an increased membrane fouling, as evidenced by the lower J/J<sub>w</sub> parameter. On  
346 this basis it can be assumed that pH 9.2 and a polymer/As ratio 30 are optimal conditions for As(V)  
347 complexation/removal by using the PolyDADMAC polymer. Considering that C% is about 100%, this ratio  
348 corresponds to a maximum loading of the polymer of about 33 mg As(V) / g<sub>polymer</sub> at pH = 9.2. Increasing the  
349 ratio to 40 the [As]<sub>p</sub> is not further reduced indicating a low tendency to shift to right the complexation  
350 equilibrium when As concentration is too low. It must be noticed that permeate concentration is above the  
351 WHO limit (10 µg L<sup>-1</sup>). This happens with a feed at As(V) concentration of 10 mg L<sup>-1</sup>, which has been used in  
352 our tests, but it must be considered that values of 2 mg L<sup>-1</sup> or lower are usually found in water to be treated  
353 and that As feed can be switched to another stock of fresh polymer when this has been completely loaded.

354

355 **Table 3:** Results of the DF-vr tests at fixed pH = 9.2 by changing the polymer/arsenic weight ratio  
 356 ([PolyDADMAC] = 200/300/400 mg L<sup>-1</sup>; [As(V)] = 10 mg L<sup>-1</sup>; TMP = 200 kPa, T = 25 ± 1 °C).

	Polymer/As weight ratio		
	20	30	40
[As] <sub>p</sub> (μg L <sup>-1</sup> )	30	15	15
C%	99.7	99.9	99.9
R% TOC	98.1	99.0	98.7
J/J <sub>w</sub>	0.71	0.66	0.58

357

358 Since the pH of As polluted water is normally in the range 7-8, in order to minimize the use of chemicals  
 359 involved in the CP-UF process, some DF-vr tests were carried out using a polymer/As ratio 30 and pH 7.5 to  
 360 check the performance of the system. Obtained results, summarized in Table 4, evidenced that by  
 361 operating at pH 7.5 a five times higher concentration into the permeate was obtained with respect to pH  
 362 9.2 showing the importance of pH control.

363

364 **Table 4:** Results of the DF-vr test at fixed polymer/arsenic weight ratio = 30 at different pH ([PolyDADMAC]  
 365 = 300 mg L<sup>-1</sup>; [As(V)] = 10 mg L<sup>-1</sup>; TMP = 200 kPa, T = 25 ± 1 °C).

	pH	
	7.5	9.2
[As] <sub>p</sub> (μg L <sup>-1</sup> )	75	15
C%	99.3	99.9
R% TOC	98.4	99.0
J/J <sub>w</sub>	0.64	0.66

366

### 367 3.1.3. Comparison of PDEHED and PolyDADMAC polymers performance

368 To compare the performance of the two considered polymers under the same operating mode, some DF-vr  
 369 tests were carried out by using the PDEHED polymer at the optimal chemical condition previously  
 370 determined: pH = 7.5 and polymer/As ratio = 20. The results, reported in Table 5, in comparison with that  
 371 one obtained by using the PolyDADMAC under its optimal conditions, show that the two polymers  
 372 permitted to obtain the same performance in term of As complexation and As concentration in the  
 373 permeate, while TOC rejection and membrane fouling were practically identical. From an economical and  
 374 environmental point of view an advantage in using the PDEHED polymer could be represented by the  
 375 operation at pH = 7.5, which is compatible with the pH of As polluted water, thus avoiding or minimizing  
 376 the use of chemicals to correct the pH upstream and downstream the CP-UF process.

377

378 **Table 5:** Comparison of the results of the DF-vr tests by using the two polymers under the respective  
379 optimal chemical conditions ( $[As(V)] = 10 \text{ mg L}^{-1}$ ; TMP = 200 kPa, T =  $25 \pm 1 \text{ }^\circ\text{C}$ ).

Polymer	pH	Polymer/As weight ratio	C%	R% TOC	$[As]_p$ ( $\mu\text{g L}^{-1}$ )	J/J <sub>0</sub>
PDEHED	7.5	20	99.9	98.4	15	0.68
PolyDADMAC	9	30	99.9	99.0	15	0.66

380

381 Concerning the comparison of the two different operating DF mode (continuous and with volume  
382 reduction), the same optimum operating conditions were obtained by using the PDEHED polymer (pH 7.5  
383 and polymer/As ratio = 20), but a higher As concentration in the permeate ( $15 \mu\text{g L}^{-1}$ ) was obtained by  
384 operating in DF-vr mode owing to a greater retentate concentration.

385

### 386 3.1.3. Comparison of the CP-UF process with literature data

387 In table 6 the conditions and results of the present work obtained in the CP-UF tests are compared with  
388 that one of the Rivas group (Rivas et al., 2006, 2010; Palencia et al., 2009) which applied a very similar CP-  
389 UF process (named from the authors liquid-phase polymer based retention (LPR)), in the separation of  
390 arsenic ions from water using the same type of polymer. A brief survey of the experimental results  
391 obtained by the Rivas group is reported in the supporting information. The most important difference is the  
392 polymer/As molar ratio: Rivas et al. used a polymer/As molar ratio of 20, which is 1330 times higher than  
393 the value used in the present work. It must be considered that fouling is a major drawback of membrane  
394 filtration, revealing itself as a decline in flux over operation time. A significant higher fouling can be  
395 expected by using a high polymer/As ratio, but a direct comparison in terms of permeate flux cannot be  
396 reported because this data is missing.

397 The not complete As removal (see Table 6) obtained in the present work can be ascribed to the higher  
398 MWCO of the membrane used in the CP-UF step (PES 30 kDa), the lower polymer amount and the absence  
399 of polymer pre-treatment to remove the smaller polymer chains present in the poly-disperse commercial  
400 polymer.

401

402

403

404

405

406 **Table 6:** Comparison of the results obtained in this work with the literature data (Rivas et al., 2006, 2010;  
 407 Palencia et al., 2009) using the polymer PolyDADMAC.

Membrane	Pressure (bar)	UF Mode	Polymer/As molar ratio	C%	[As] <sub>perm</sub>	Permeability (L h <sup>-1</sup> m <sup>-2</sup> bar <sup>-1</sup> )
PES 10 kDa*	3.5	DF-c	20	100%	Not reported	Not reported
PES 30 kDa**	2	DF-vr	0.015	99.9 %	15 µg L <sup>-1</sup>	62.22

408 \* Literature; \*\* this work

409

### 410 3.2. Tests performed in DF-vr mode on As(III) solutions

411 As previously reported, on the basis of As(III) speciation, at pH < 9.2 the arsenite is uncharged, thus unable  
 412 to interact with polymers which works by an ionic exchange mechanism. This means that As(III) could not  
 413 be separated by the CP-UF, thus requiring its oxidation into the more easily extractable As(V) form as first  
 414 step to obtain an efficient As removal process.

415 To experimentally verify the absence of As(III) complexation under the optimal conditions previously  
 416 determined, some tests were performed in DF-vr mode under the operating conditions reported in Table 5  
 417 using as feed [As(III)] = 10 mg L<sup>-1</sup>.

418 Obtained results confirmed that arsenite was not complexed/separated (C% = 0 and R%(TOC) > 98%) by the  
 419 two polymers considered in the present work, thus requiring a pre-oxidation process to effectively remove  
 420 all As species from contaminated water.

421

### 422 3.3. Photocatalytic oxidation of As(III) to As(V)

#### 423 3.3.1. Theoretical considerations and adsorption tests of As(V) and As(III) on TiO<sub>2</sub> photocatalyst

424 Photocatalytic oxidation with TiO<sub>2</sub> for converting As(III) to As(V) has been studied by some research groups  
 425 (Guan et al., 2012; Yang et al., 1999). A brief summary of the literature study containing the detailed  
 426 theoretical consideration on the photocatalytic oxidation of As(III) to As(V), which permitted to identify the  
 427 previous operating conditions, are reported in supporting information.

428 Photocatalytic oxidation tests of As(III) to As(V) were performed under the following operating conditions:

429 i) [As(III)]<sub>in</sub> = 10 mg L<sup>-1</sup>; ii) [TiO<sub>2</sub>] = 0.05 g L<sup>-1</sup>; iii) pH = 9; iv) O<sub>2</sub> bubbling.

430 These conditions were chosen on the basis of the pertinent literature. The pH 9 was chosen considering  
 431 that: i) the difference between the redox potential of the As(V)/As(III) couple ( $E_{As(V)/As(III)}$ ) and the valence  
 432 band potential ( $E_{VB}$ ), which is the thermodynamic driving force for the photo oxidation process, increases  
 433 with increasing pH (2.52 vs. 2.75 V at pH 3 and 9, respectively) (Bissen et al., 2001; Lee and Choi, 2002); ii)  
 434 the process of adsorption of As(III)/desorption of As(V), caused by the electrostatic interaction between  
 435 catalyst surface and As(III) or As(V) ion, is favored at alkaline pHs (Zheng et al., 2010).

436 0.05 g L<sup>-1</sup> photocatalyst concentration and air bubbling were chosen sine they promote As(III) oxidation to  
437 As(V), giving better O<sub>2</sub> dispersion into the reaction environment (Jayaweera et al. (2003)) and limiting light  
438 scattering by photocatalyst particles (Ferguson et al., 2005; Molinari et al., 2013).

439 Some tests were carried out for evaluating the adsorption of As(III) and As(V) at pH 4 and 9 on 0.5 and 1.0 g  
440 L<sup>-1</sup> of TiO<sub>2</sub>. Obtained results, summarized in Table S1 in the case of As(V), confirmed that As(V) species were  
441 not adsorbed by TiO<sub>2</sub> at pH = 9, because of electrostatic repulsion, while 5.0 mg of As(V) per g of  
442 photocatalyst were adsorbed at acidic pH = 4. In the case of As(III), the results confirmed that As(III) was  
443 adsorbed by TiO<sub>2</sub> at both alkaline and acidic pHs, with a higher extent at pH = 4 (Table S2). The ratio mg  
444 As(III)<sub>ads</sub> / g TiO<sub>2</sub> = 4.0 obtained at pH = 9 is in agreement with the results reported by Dutta et al. (2004),  
445 which found at pH = 9 a TiO<sub>2</sub> adsorption capacity of 3.9 ± 2.4 mg of arsenite per g of TiO<sub>2</sub>.

446

### 447 3.3.3. Photocatalytic tests

448 The photocatalytic oxidation of As(III) to As(V) was carried out in the experimental set-up reported in Fig.  
449 S1.

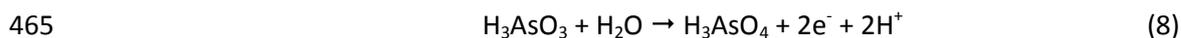
450 The methodology to analyze As(III) and As(V) in the solutions submitted to photocatalysis is reported in  
451 Scheme 1 and explained in the following.

452 The experimental evidence that As(III) is not complexed by the polymer in the range 7.5-9.2 has been used  
453 for analytical purposes for As speciation (i.e. discrimination between As(III) and As(V)). In particular, an  
454 analytical procedure was implemented by coupling the analytic methods (Merckoquant analytic kits and ICP-  
455 OES) with the CP-UF technique because both of them did not permit to distinguish between As(III) and  
456 As(V). The basic idea of this procedure consists in submitting a feed solution containing As to the CP-UF  
457 process under the optimal chemical conditions previously determined. As(III) species are not complexed  
458 and pass in the permeate, as experimentally verified, while As(V) species are complexed and retained by  
459 the membrane. On the basis of this, the analysis of the permeate permits to determine As(III) concentration  
460 while As(V) concentration can be determined as:

$$461 \quad [As(V)] = [As]_{total} - [As(III)] \quad (7)$$

462 where [As]<sub>total</sub> represents total arsenic concentration in the feed solution.

463 During the photocatalytic tests the pH of the aqueous solution decreased because As(III) was oxidized to  
464 As(V) by the following reaction:



466 Two moles of H<sup>+</sup> are developed per mole of As(III) oxidized to As(V) while the electrons reduced the oxygen  
467 blown into the solution. Besides, the formed As(V) species dissociates producing other H<sup>+</sup> ions.

468 Because of the pH decrease, to avoid that the photo-produced As(V) was absorbed by the photocatalyst  
469 particles and retained during the microfiltration (MF) of the samples on the GH-polypro membrane, the pH

470 of each sample withdrawn from the photoreactor was adjusted to 9 prior to MF. The total As concentration  
 471 (As(III) + As(V)) measured after this MF step was still 10 mg L<sup>-1</sup>, showing the positive effect of pH correction.  
 472 For arsenic speciation a volume of 13 mL of a PolyDADMAC solution 2000 mg L<sup>-1</sup> was added to 87 mL of  
 473 each micro-filtered sample withdrawn during the photo-oxidation tests, thus obtaining 100 mL of solution  
 474 at polymer/As ratio of 30 and pH = 9, that are the optimal operating conditions previously determined for  
 475 the considered polymer. Taking into account this dilution, the total As concentration of each photo-  
 476 oxidation sample submitted to the CP-UF “speciation” step decreased to 8.7 mg L<sup>-1</sup> showing that no As was  
 477 lost but only oxidized from As(III) to As(V). The PolyDADMAC polymer was preferred to PDEHED, since it  
 478 works at pH 9, which is the pH of the micro-filtered samples.  
 479 The CP-UF “speciation” tests were performed in DF-vr mode. As concentration in the permeate was  
 480 measured and then taking into account the initial dilution the concentration of As(III) and As(V) during the  
 481 photocatalytic tests have been calculated. The results are reported in Table 7 while in Fig. 5 the trend of  
 482 As(III) and As(V) concentrations during a photocatalytic run is reported.

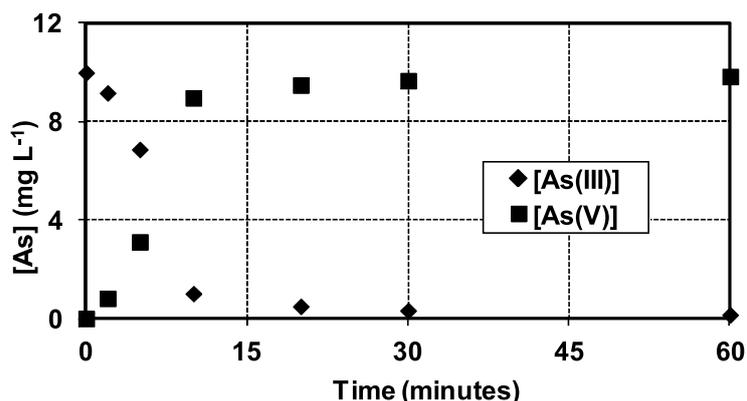
483

484 **Table 7.** Results of the photo-oxidation of As(III) to As(V) (As(III)<sub>in</sub> = 10.0 mg L<sup>-1</sup>, pH<sub>in</sub> = 9.0, TiO<sub>2</sub> = 0.05 g L<sup>-1</sup>,  
 485 O<sub>2</sub> = 22 ppm, T = 30 ± 1 °C).

Time (minutes)	pH	[As(III)] <sub>perm</sub> (mg L <sup>-1</sup> )	[As(III)] <sub>perm</sub> = [As(III)] <sub>fed,CP-UF</sub> (mg L <sup>-1</sup> )	[As(V)] <sub>fed,CP-UF</sub> (mg L <sup>-1</sup> )	[As(III)] <sub>photo</sub> (mg L <sup>-1</sup> )	[As(V)] <sub>photo</sub> (mg L <sup>-1</sup> )	Conversion (%)
0	9.05						0
2	7.89	8.00	7.985	0.715	9.178	0.822	8.22
5	6.97	6.00	5.985	2.715	6.879	3.12	31.21
10	5.33	0.90	0.885	7.815	1.017	8.983	89.83
20	4.72	0.45	0.435	8.265	0.500	9.500	95.00
30	4.90	0.30	0.285	8.415	0.328	9.672	96.72
60	4.85	0.15	0.135	8.565	0.155	9.845	98.45

486

487



488

489 **Fig. 5.** Results of the photo-oxidation of As(III) to As(V) ( $As(III)_{in} = 10.0 \text{ mg L}^{-1}$ ,  $pH_{in} = 9.0$ ,  $TiO_2 = 0.05 \text{ g L}^{-1}$ ,  $O_2$   
 490  $= 22 \text{ ppm}$ ,  $T = 30 \pm 1 \text{ }^\circ\text{C}$ ).

491

492 The reaction was very fast in the time interval 0-10 minutes (see Fig. 5). Indeed at 10 min As(III)  
 493 concentration was  $1.017 \text{ mg L}^{-1}$ , corresponding to ca. 90 % conversion. In this time interval, As(III)  
 494 concentration decreased linearly, with a trend described by the following straight line:

$$495 \quad [As(III)]_{photo} = -0.83 t + 10 \quad (9)$$

496 where  $t$  is the time (minutes), and the obtained regression factor was  $r^2 = 0.95$ .

497 For a zero order kinetics the reaction rate can be expressed as

$$498 \quad r = -\frac{d[As(III)]}{dt} = k \quad (10)$$

499 By integrating this equation in the time interval 0-10 minutes, eq. (9) is obtained, where  $r = k = 0.83 \text{ mg}_{As(III)} \text{ L}^{-1} \text{ min}^{-1}$ . Then in this time interval the system proceed with a zero order kinetics with respect to As(III)  
 500 concentration indicating most likely that the photo-oxidation of As(III) to As(V) took place under  
 501 photocatalyst saturation conditions.  
 502

503 In the time interval 10-60 minutes the photo-oxidation process was very low. This trend could be ascribed  
 504 to the previously observed pH decrease, which resulted in less favorable conditions for the photo-oxidation  
 505 process and the very low As(III) concentration. Initially the  $pH = 9$  favored the As(III) adsorption and As(V)  
 506 desorption, and As(III) concentration was high while As(V) concentration was low, resulting in the high  
 507 observed kinetic rate. At 10 minutes the  $pH = 5.33$ , and the electrostatic interaction between the positively  
 508 charged  $TiO_2$  and the negatively charged As(V) species are disadvantageous for the produced As(V) release,  
 509 giving a photocatalyst inhibition by the product and the resulting kinetic slowdown. During this time  
 510 interval the photocatalytic oxidation of As(III) to As(V) proceed with a first-order kinetics with respect to  
 511 As(III). Indeed As(III) decreased with a trend described by the following equation:

$$512 \quad \ln [As(III)]_{photo} = -0.0424 t + 0.441 \quad (11)$$

513 with a regression factor  $r^2 = 0.90$ , evidencing a first-order kinetic constant of  $0.0424 \text{ min}^{-1}$ , comparable with  
 514 that one obtained in literature (Yan et al., 2016).

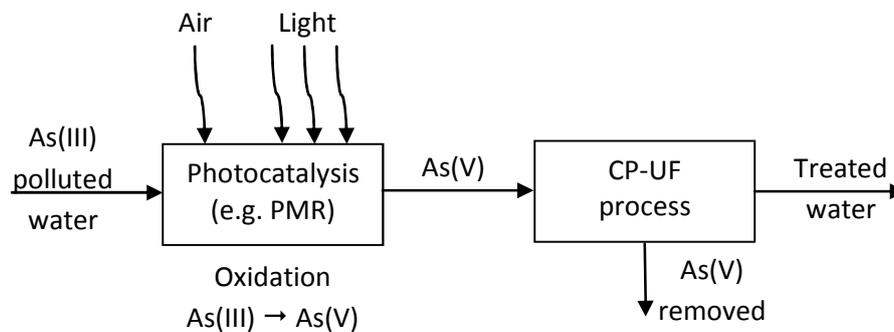
515 At the end of the photocatalytic process (60 minutes) the conversion was 98.45%, corresponding to an  
516 As(III) concentration of  $0.155 \text{ mg L}^{-1}$ , which was higher than the WHO limit. The use of a higher  
517 photocatalyst amount and a better pH control during the photo-oxidation process, to avoid photocatalyst  
518 inhibition by the product, could permit to achieve lower As(III) residual concentration.

519

#### 520 **4. Conceptual scheme of the photocatalysis and CP-UF coupling and some criteria to operate the CP-UF** 521 **process**

522 In Fig. 6 a conceptual coupling between the photocatalytic and the CP-UF process is reported. The  
523 photocatalytic step, as has been shown, can be effectively used to oxidize As(III) to As(V). The tests were  
524 carried out in a batch photoreactor but for process application a photocatalytic membrane reactor will give  
525 the advantages already studied for this type of photoreactor (Jiang et al., 2016; Mozia et al., 2015).

526



527

528

529 **Fig. 6.** Conceptual coupling of photocatalysis and CP-UF (PMR = Photocatalytic Membrane Reactor).

530

531 The CP-UF process involves two steps: complexation of the target species (in this case As(V)) to the polymer  
532 till reaching the maximum loading capacity and then the decomplexation for regenerating and recycling the  
533 polymer. Each one of the two diafiltration methods before described can be useful for application  
534 purposes. The diafiltration in continuous (DF-c) can be useful for loading the polymer by continuous feeding  
535 of the aqueous solutions containing the pollutant. The diafiltration with volume reduction (DF-vr) can be  
536 useful for regenerating the polymer and its conditioning to the optimum pH.

537 Indeed in the DF-c, because the retentate volume does not change, the permeate flow rate should remain  
538 constant provided a suitable polymer concentration and stirring rate are chosen.

539 In the DF-vr, for regenerating the polymer, the initial volume is reduced by half and then a solution at pH  
540 suitable for decomplexation can be added. The DF-vr is continued with a series of volume reduction and  
541 solution addition till reaching a complete pollutant release. This method permits to save the volume of  
542 washing solution. Indeed, from the theory of diafiltration with a membrane having 0% retention to the  
543 species to remove, 7 DV (diafiltration volume) are required to remove the 99.9% of the pollutant by using

544 the DF-c, while 10 DV are required for removing the same percentage by using the DF-vr. But it must be  
545 considered the definition of DV which is  $DV = V_i$  (initial volume) in the case of DF-c and  $DV = V_i / 2$  in the  
546 case of DF-vr so, in this last case, the required volume is 5 times the initial.

547 The exposed concepts and criteria will be helpful in the prosecution of this work to address the research on  
548 the process application.

549

## 550 **5. Conclusion**

551 In the present work the possibility to couple the photocatalytic oxidation of As(III) to As(V) and the  
552 complexation-ultrafiltration (CP-UF) process for arsenic removal from contaminated water has been  
553 studied.

554 In the CP-UF step the performance of two polymers, poly(dimethylamine-coepichlorohydrin-  
555 coethylenediamine) (PDEHED) and poly(diallyl dimethyl ammonium chloride) (PolyDADMAC), have been  
556 evaluated by determining the best operating conditions (pH and polymer/As weight ratio). pH = 7.5 and  
557 polymer/As ratio = 20 have been found to be the optimal for As(V) removal by using the PDEHED polymer.  
558 Higher values (pH = 9 and polymer/As weight ratio = 30) were needed by using the PolyDADMAC polymer.  
559 These results show that the type of polymeric agent influences both the considered parameters. The  
560 selection between the two tested polymers depends on the pH of the polluted water to be treated: in the  
561 range 7-8 the polymer PDEHED showed better performance, while at higher pH the PolyDADMAC was  
562 preferable. No As(III) removal was observed by operating under the optimal chemical conditions regardless  
563 the polymer, confirming the need of a pre-oxidation process to effectively remove As(III) species from  
564 contaminated water.

565 Photocatalytic oxidation of As(III) to As(V) was successfully performed under UV radiation by using  $\text{TiO}_2$   
566 ( $0.05 \text{ mg L}^{-1}$ ) as the photocatalyst,  $\text{O}_2$  as the oxidant and pH = 9. A speciation method, using in this case the  
567 CP-UF process for analytical purposes, was used to evaluate As(III) conversion to As(V). The results showed  
568 that the reaction was very fast in the time interval 0-10 minutes (average reaction rate of  $7.83 \times 10^{-1} \text{ mg}_{\text{As(III)}} \text{ L}^{-1} \text{ min}^{-1}$ ).  
569 In this time interval, As(III) concentration decreased linearly, indicating that the photo-oxidation  
570 of As(III) to As(V) took place under photocatalyst saturation conditions. In the following 50 minutes the  
571 photo-oxidation process was very slow, with a lower average reaction rate ( $2.49 \times 10^{-2} \text{ mg}_{\text{As(III)}} \text{ L}^{-1} \text{ min}^{-1}$ ).  
572 This trend was ascribed to both pH and As(III) concentration decrease during the photo-oxidation process.  
573 The overall results show that the combination of the photocatalytic oxidation of As(III) to As(V) and the CP-  
574 UF process permit to obtain a quite complete arsenic removal from the treated water although some  
575 improvement is still needed. Use of a membrane with lower MWCO, higher polymer amount and/or  
576 polymer pre-filtration could increase the performance of the CP-UF step, while the use of a higher  
577 photocatalyst amount and a better pH control during the photo-oxidation process, could increase the

578 performance of the photocatalytic step. The suitable use of the continuous diafiltration and the diafiltration  
579 with volume reduction are other aspects that can address the CP-UF process towards process application.

580

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