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1   **Electrospun polyethylene terephthalate (PET) nanofibers as a new adsorbent for solid**

2   **phase microextraction of chromium (VI) in environmental water samples**

3

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6

7   **Abstract**

8   In this study, polyethylene terephthalate (PET) nanofiber film was fabricated by a simple and

9   low-cost electrospinning method and used as a novel adsorbent for solid phase microextraction

10   (SPME) of chromium (VI) in water samples. 1,5-Diphenylcarbazide (DPC) as a selective

11   complexing agent for Cr(VI), and sodium dodecyl sulfate (SDS) as a surfactant were added to

12   sample solutions to improve the selectivity and sensitivity of the method. The extraction

13   procedure was coupled with UV-Vis spectrophotometry for determination of preconcentrated

14   Cr(VI). The influence of main parameters that affect the recovery of Cr(VI) including desorption

15   conditions, pH, adsorbent dosage, adsorption time, and concentration of DPC and SDS were

16   studied and optimized. The analytical figures of merit of the method were: preconcentration

17   factor, 125; linear dynamic range, 1.8-60 ng mL^{-1}; determination coefficient (R^2), 0.9923; limit

18   of detection (LOD), 0.6 ng mL^{-1}, and limit of quantification (LOQ), 1.8 ng mL^{-1}. The relative

19   standard deviations (RSD%) for intraday and interday assays were 1.6% and 3.1% (n=3),

20   respectively. The proposed method was successfully applied for determination of Cr(VI) in

21   natural water samples, and the relative recoveries in 96.9-99.1% range were obtained.

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22   **Keywords:** Polyethylene terephthalate nanofibers; Solid phase microextraction; Chromium (VI);

23   1,5-Diphenylcarbazide; Water samples.

24

Introduction

26   Heavy metals are ranked as highly toxic elements in the environment. They can enter a water

27   supply by industrial and consumer wastes, or even from acidic rain breaking down soils and

28   releasing heavy metals into waters. These metals tend to bioaccumulate in food chain and exert

29   various health effects on humans. [1-5]Chromium (Cr) occurs in the environment primarily in two

30   oxidation states: Cr (III) which occurs naturally and is an essential nutrient, and Cr (VI) that is

31   toxic and most commonly produced by industrial processes. The body can detoxify some amount

32   of Cr (VI) to Cr (III).[6,7]   However, trace levels of Cr(VI) is the object of strict health official

33   norms in drinking water up to 1 ng mL^{-1}. Accordingly, the trace determination of Cr(VI) in

34   natural water is essential in environmental pollution monitoring.[8-10] A method for selective

35   measurement of this metal is based on spectrophotometric determination of Cr(VI) after reaction

36   with 1,5-diphenylcarbazide (DPC).[11,12] However, because concentrations of Cr(VI) in the

37   environmental water samples are usually below detection limit of this technique, direct

38   quantification of this element seems to be problematic. Therefore, a sample preparation step

39   before the analysis is required.

40   In recent years, the use of electrospun polymeric nanofibers for adsorption of heavy metals

41   has increased.[13-30] Polymeric nanofibers can be fabricated by a number of techniques such as

42   drawing,   template   synthesis,   phase   separation,   self-assembly,   and   electrospinning.

43   Electrospinning is a remarkably simple method for producing nanofibers of a wide variety of

44   polymers. This is a process that creates nanofibers through an electrically charged jet of polymer

45   solution or polymer melt. [31] The basis of this technique is similar to electrospray ionization. [32]

46   Recently, electrospun nanofibers have been used as adsorbent in solid phase extraction (SPE) [31-

47   35] and micro-SPE. [36,37] Since the surface area per unit volume is inversely proportional to the

48   diameter of nanofibers, thus the smaller the diameter, the greater is the surface area per unit

49   volume.[38] Moreover, the porous structure of nanofibers increases hydrophilicity of the surface

50   and provides more paths for diffusion of analyte, and thus facilitates better interaction between

51   the adsorbent and the analyte(s).

52   In the present work, the electrospun polyethylene terephthalate (PET) nanofiber film was

53   fabricated and introduced as a new type of polymeric adsorbent for selective extraction of Cr(VI)

54   in the presence of DPC and SDS. To the best of our knowledge this is the first time that PET has

55   been used for thin film microextraction of chromium (VI).

56

Experimental

Materials and Reagents

59   All chemicals used were of analytical grade. Ethanol (EtOH), potassium dichromate

60   ($K_2Cr_2O_7$), acetone, sulfuric acid (H_2SO_4), sodium chloride (NaCl), Iron (III) chloride

61   hexahydrate, copper (III) nitrate, ammonium molybdate tetrahydrate, 1,5-diphenylcarbazide

62   (DPC), mercury (II) chloride, sodium dodecyl sulfate (SDS), and polystyrene were purchased

63   from Merck Chemicals (Darmstadt, Germany). Polyethylene terephthalate (PET) and methanol

64   (MeOH) were prepared from Sigma Aldrich Ltd (St Louis, USA). Trifluoroacetic acid (TFA)

65   (99%) was obtained from Samchun Pure Chemical (Pyeongtaek, South Korea). The stock

66   standard solution of Cr (VI) (1000 μg mL^{-1}) was prepared by dissolving a weighted amount of

67     $K_2Cr_2O_7$ in distilled water and stored at 4 °C. The working standard solutions of Cr (VI) were

68   prepared daily by appropriate dilution of the stock solution with distilled water. The DPC

69   solutions were prepared daily in MeOH at the concentration level of 10^{-2} mol L^{-1}.

70

71   **Instrumentation**

72   A double beam Rayleigh UV-2601 (Beijing, China) UV-Vis spectrophotometer, using a

73   couple of 1-cm optical pathlength micro-cuvette (Fisher Scientific, USA), was utilized for

74   spectrometric determination of chromium (VI) complex. A Heidolph magnetic stirrer model MR

75   3001 K (Schwabach, Germany) was used for mixing the solutions. An Eurosonic 4D (Euronda,

76   Montecchio Precalcino (Vincenza) Italy) ultrasonic water was used for desorption process. The

77   pH values were measured with a WTW Inolab 720 pH meter (Weilheim, Germany). The

78   morphology of electrospun nanofibers was characterized by scanning electron microscopy

79   (SEM) (Zeiss DSM-960 Oberkochen, Germany) at an accelerating voltage of 15 KV. The

80   infrared transmittance spectra were obtained with an Equinox 55 FT-IR spectrometer (Bruker,

81   Bremen, Germany) in the 400-4000 cm^{-1} region. The specific surface area and average pore

82   diameter of the electrospun PET were measured with a Brunauer-Emmett-Teller (BET) surface

83   area analyzer (BELCAT-A, Japan).

84

85   **Nanofibers fabrication**

86   The electrospinning set-up consisted of a direct current (DC) high voltage power supply, a

87   syringe pump (SP 1000), and a collector fabricated by Fanavaran Nano-Meghyas (FNM, Tehran,

88   Iran) was used to produce nanofibers. The DC voltage supply had an electrical potential range of

89   0-25 kV. The feed rate of the polymer solution was regulated by using a programmable two

90   channel syringe pump. The flow rate of the pump could be varied between 0.02 µL h^{-1} and 0.064

91   mL h^{-1}. In this work, a 2 mL syringe (Soha, Alborz, Iran) with a needle diameter of 0.2 mm was

92   used and the voltage (15 kV) was applied between the tip of the syringe and ground collector.

93   Electrospun fibers were collected on a metal collector, connected with an aluminum foil placed

94   at a distance of 10 cm from the tip of the syringe's needle, at a flow rate of 0.3 mL h^{-1}. The

95   polymer solution was prepared by dissolving appropriate amounts (0.18 g) of PET in 1 mL of

96   TFA (18% w/v). The solutions were electrospun for two hours in all the experiments. After

97   electrospinning completed, the aluminum foil were floated in MeOH to separate the adsorbent

98   from the foil before use. The setup of electrospinning is illustrated in Fig. 1.

99   Fig. 1

100   **The procedure**

101   Firstly, 25 mL of Cr(VI) solution (25 ng mL^{-1}) was placed in a beaker and 0.5 mL of sulfuric

102   acid (0.5 mol L^{-1}) was added to it (pH 1.7). Then, 150 μL of a methanolic solution of DPC (0.01

103   mol L^{-1}) was added to the mixture and stirred for 5 min. After that, 5 mg of SDS (0.5 mL of

104   aqueous solution, 1% w/v) and 5 mg of the adsorbent were added to the solution and stirred for

105   20 min. Thereafter, the adsorbent was removed from the solution and carefully transferred to a

106   0.5 mL safe-lock Ependorph. Then, 200 μL of EtOH (eluent) was added to the adsorbent and

107   ultrasonicated for 5 min. Finally, absorbance of the solution was measured at 543 nm using UV-

108   vis spectrophotometer.

109

110   **Results and discussion**

111   **Characterization of PET nanofibers**

112   The SEM micrographs of the electrospun nanofibrous PET is shown in Fig. 2. The structure is

113   composed of numerous, randomly oriented three-dimensional nonwoven nanofibers with

114   uniform diameters in the range of 98-504 nm. Figure 2 displays the FT-IR transmittance

115   spectrum of the PET nanofibers. The strong band at 1727 cm^{-1} is assigned to stretching vibration

116   of C=O. The peaks at 3068, 2960 and 730 cm^{-1} are ascribed to C-H aromatic and aliphatic

117   vibrational stretching, and out of plane C-H bending, respectively. Moreover, the bands at 1112

118   and 1260 cm^{-1} are due to C-O stretches. The specific surface area and average pore diameter of

119   the electrospun PET were measured with a Brunauer-Emmett-Teller (BET) surface area analyzer

120   and found to be equal to 1.67 m^2/g and 11.8 nm, respectively.

121   Fig. 2

122   **Effect of desorption conditions**

123   After adsorption of the Cr(VI)-DPC complex onto the PET nanofibers was completed, an

124   appropriate solvent is required for elution of the complex from surface of the nanofibers prior to

125   spectrophotometry analysis. The recovery percentage of Cr(VI)-DPC, which is calculated using

126   Eq. (1), is highly dependent on desorption solvent type and volume. Therefore, a suitable solvent

127   should be selected that dissolves well the adsorbed Cr(VI)-DPC.

128                    $$ER = \frac{C_f v_f}{C_i v_i} \times 100 \qquad\qquad (1)$$

129   Where C_f is the concentration of analyte in desorption solvent, C_i is the concentration of

130   analyte in the initial sample solution, and V_i and V_f are the volume of initial sample solution and

131   volume of desorption solvent, respectively. Regarding the polarity of DPC[39], the solvents such as

132   acetone, MeOH, and EtOH were tested as desorption solvents with the proposed procedure.

133   According to the results, the following order of elution power was achieved:

134   acetone>EtOH>MeOH. Although among these solvents the highest extraction efficiency was

135   obtained using acetone, but because it is highly evaporative, EtOH with much lower volatility

136   and toxicity was preferred to be used as the desorption solvent for subsequent experiments (Fig.

137 3a). In the next step, the effect of eluent (EtOH) volume was investigated in 100-350 μL range.

138 The maximum efficiency was obtained using 200 μL EtOH with the standard deviation of 0.0035

139 (n=2) (Fig. 3b). Thus, 200 μL of EtOH was adopted for further experiments.

140 After adding the optimized volume of desorption solvent to the adsorbent, it was subjected to

141 ultrasound for an appropriate time to speed up desorption of Cr(VI)-DPC. Since recovery of the

142 analyte is greatly dependent on desorption time (ultrasonication time), the effect of this

143 parameter was studied in the range of 1-15 min according to the proposed procedure. Figure 3b

144 shows that maximum efficiency was obtained in 5 min ultrasonication, thus it was chosen as the

145 optimum desorption time.

146 Fig. 3

147 **Effect of pH**

148 The complexation reaction between Cr(VI) and DPC occurs in strongly acidic media, and thus

149 is a pH dependent process. The influence of pH of the sample solution on the performance of the

150 method was studied in the range of 0.9-2.1. At higher pH values, the reaction is slow.[40] The pH

151 was adjusted using H_2SO_4 (0.5 mol L^{-1}) and the experiments were carried out with the procedure

152 in section 2.4. Figure 4 shows that the absorbance increased with increasing pH from 0.9 up to

153 1.7 and then decreased at higher values. This observation can be attributed to the fact that the

154 rate of formation of Cr(VI)-DPC complex is dependent on the pH of sample solution. Since the

155 maximum efficiency was obtained at pH 1.7, it was selected as the optimum value.

156 Fig. 4

157 **Effect of diphenylcarbazide concentration**

158 Chromium (VI) can react with DPC in a strongly acidic solution (pH, 1.7) to form the reddish

159 violet Cr-diphenylcarbazone complex, which is carbazone inner salt of a chromous ion. This

160 reaction is highly specific for Cr(VI) versus Cr(III), and the product can be detected by

161 spectrophotometric analysis at λ_{max} of about 540 nm.[41] Therefore, the influence of ligand (DPC)

162 concentration on the efficiency of the complexation process was studied in the range of 2×10^{-5} to

163 10×10^{-5} mol L^{-1}. As can be seen in Fig. 4, the absorbance increased with increasing concentration

164 of DPC and yielding a maximum at 6×10^{-5} mol L^{-1} followed by a decline with its further increase.

165 The decrease in the absorbance at the concentrations higher than 6×10^{-5} mol L^{-1} can be ascribed

166 to the decrease in complexation efficiency due to dimerization of DPC in the sample solution.

167 Thus, insufficient DPC was accessible for formation of complex with Cr(VI).[42] Therefore, 6×10^{-5}

168 mol L^{-1} was chosen as the best concentration of DPC for complexation with Cr(VI).

169

170 **Effect of *s*odium dodecyl sulfate concentration**

171 Sodium dodecyl sulfate (SDS) is a widely used anionic surfactant that acts as a bridge

172 between the PET nanofibers and Cr(VI)-DPC complex, and thus plays an important role in the

173 extraction of the analyte. The effect of SDS concentration on the extraction efficiency was

174 studied in 2-6mg (200 to 600 μL, 1% w/v) range with the procedure in section 2.4. Figure 5

175 shows that with increasing SDS up to 5 mg the absorbance increased, and then decreased with

176 more adding SDS to the sample solution. The corresponding drop in the absorbance can be

177 explained by the self-aggregation of SDS molecules at higher concentrations in sample solution.

178 Accordingly, 5 mg was selected as the optimum amount of SDS in the proposed procedure.

179   Fig. 5

180 **Effect of adsorbent type and dosage**

181 The adsorbent is a crucial factor in solid phase microextraction that has very significant effect

182 on the extraction efficiency. Different polymers such as PET, polystyrene, and nylon6,6 were

183   electrospun and, their fabricated nanofibers, tested as adsorbent in accordance with the proposed

184   procedure. The results showed that among these polymers, PET was the most effective adsorbent

185   toward Cr(VI)-DPC complex. After selection of nanofibrous PET as an appropriate adsorbent in

186   solid phase microextraction of Cr(VI), the influence of PET dosage was also investigated in 2 to

187   7 mg range. Figure 5 shows that with increasing amount of PET in the sample solution up to 5

188   mg, the absorbance was increased and after that reduced. The decline of the absorbance at the

189   amounts higher than 5 mg may be attributed to this fact that the volume of added eluent in

190   desorption step was insufficient for removing all of Cr(VI)-DPC complex. Therefore, 5 mg of

191   nanofibrous PET was recognized as the optimum amount in extraction of the analyte.

192

193   **Effect of extraction time (stirring time)**

194   The extraction efficiency strongly depends on the amount of mass transfer of analyte from

195   sample solution onto adsorbent. Stirring the sample solution can speed up this process when the

196   adsorbent is contacted with the sample solution. Therefore, after adding appropriate amounts of

197   DPC (6×10^{-5} mol L^{-1}), SDS (5 mg), and PET (5 mg) into 25 mL of the sample solution (Cr(VI),

198   25 ng mL^{-1}), the effect of contact time (stirring time) was studied in the range of 5–30 min with

199   stirring the mixture at 400 rpm. The results recorded in Fig. 6, revealed that the highest

200   efficiency was obtained in 20 min, thus this time was chosen as the optimum stirring time.

201   Fig. 6

202   **Salt effect**

203   The influence of ionic strength of sample solution on the extraction efficiency was

204   investigated with adding NaCl in the concentration range of 0–10%, w/v. The results represented

205   in Fig. 6 showed that with increasing the concentration of NaCl in the sample solution, efficiency

206   of the method was continuously decreased. This decrease can be due to increasing the solubility

207   of Cr(VI)-DPC complex with adding NaCl to the sample solution (salting-in effect). Therefore,

208   the method was adopted without adding salt to the sample solution.

209

210   **Influence of coexisting ions**

211   The species that can change the valence state of Cr(VI) and/or react with DPC to form

212   complexes may interfere with the spectrophotometric determination of Cr(VI)-DPC complex.

213   Although the reaction of Cr(VI) with DPC is highly specific versus Cr(III), but it has been

214   reported that several other cationic species *i.e.* Cu(II), Fe(III), Hg(II), Mo(VI), and V(V) may

215   react with DPC and compete with Cr(VI).[42] Therefore, the effect of these cations and some other

216   common ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, PO_4^{3-}, CO_3^{2-}, and Cl^-, that may be

217   present in environmental water samples, on the detection of Cr(VI)-DPC were studied. A

218   coexisting ion was considered as an interference ion if its presence resulted in a variation of

219   higher than 5% in the recovery. According to the results, no significant interference

220   indetermination of Cr(VI) due to the presence of the above mentioned ions was observed (Table

221   1).

222   Table1

223   **Method evaluation**

224   Under the optimized conditions (desorption solvent, EtOH, 200 µL; DPC, $6×10^{-5}$ mol L^{-1};

225   SDS, 5 mg; pH, 1.7; adsorbent, 5 mg; adsorption time, 20 min; desorption time, 5min), the

226   analytical figures of merit including LDR, R^2, LOD, LOQ, and RSDs% were evaluated. The

227   linearity of the method was investigated using the standard solutions of Cr(VI) at fourteen

228   concentration levels with two replicates at each level. The calibration curve was constructed by

229   plotting absorbance against concentrations1.8-60 ng mL^{-1} of Cr(VI) with the satisfactory

230   determination coefficient (R^2) of 0.9923 (Fig. 1S of supplementary data). The limit of detection

231   (LOD) based on a signal to noise ratio (S/N) of 3 and limit of quantification (LOQ) with S/N of

232   10 were obtained equal to 0.6 and 1.8 ng mL^{-1}, respectively. The precision of the method was

233   studied with three replicate measurements using 25 mL of Cr(VI) solution (25 ng mL^{-1}). The

234   relative standard deviations (RSD%) for intra-day (n=3) and inter-day (three consecutive days,

235   n=3) were 1.6% and 3.1%, respectively. These RSD% values indicate that the proposed method

236   is reproducible and suitable for the quantitative determination of Cr (VI) in water samples.

237   In order to examine the reusability of the PET nanofibers, the adsorbent was washed twice

238   with 1 mL methanol then with 1 mL water, and was reused for the next analysis run. In each run,

239   5 mg of the adsorbent was used for extraction of Cr(VI) in a solution of 25 ng mL^{-1} under the

240   optimal conditions. The results showed that the recoveries were higher than 90% after 5 times

241   usages.

242

243   **Analysis of real samples**

244   In order to evaluate the applicability of the developed method, the real water samples such as

245   tap water, river water (Zayandeh-rud River), ground water, and sewage water samples were

246   prepared. All water samples were filtered by a paper filter and the pH values were adjusted at 1.7

247   and spiked with Cr(VI) at two concentration levels of 10 ng mL^{-1} and 40 ng mL^{-1}. Then, the

248   water samples were extracted and analyzed in accordance with the proposed procedure. The

249   relative recoveries (RR) were calculated based on following equation:

250                 $$RR = \frac{C_{found} - C_{real}}{C_{added}} \times 100 \qquad\qquad (2)$$

251   Where C_{found} is the concentration of analyte after adding a known amount of standard in the

252   real sample, C_{real} is the concentration of analyte in the real sample, and C_{added} is the

253   concentration of standard solution that was spiked to the real sample. The obtained relative

254   recoveries, given in Table 2 are in the acceptable range of 96.9-99.1%.

255   Table 2

256   A search in literature databases was carried out to find the previously developed methods [42-51]

257   for extraction and determination of Cr(VI) and the results were summarized in Table 3. In

258   comparison, the proposed method benefits the main advantage of a remarkably simple

259   electrospinning method for producing the adsorbent as PET nanofibers. In addition, the method

260   precision (RSD%) is better than that of the other reported studies. High relative recoveries (~97-

261   99%) were obtained for extraction in 25 mL of several complex matrix samples such as tap,

262   river, sewage and ground waters. The high relative recoveries improve detection limits, simplify

263   quantification, and decrease disturbance to the system being studied. [52] The method limit of

264   detection (0.6 ng mL^{-1}) and the enhancement factor (125) are better than most other existing

265   techniques. The linear dynamic range is comparable to that of other methods. The proposed

266   procedure is faster than most of other previously developed.

267   Table 3

Conclusions

269   The simple and low-cost prepared electrospun polyethylene terephthalate (PET) nanofiber

270   film, with a large specific surface area and fine porous structure, was used as a new and excellent

271   adsorbent for solid phase microextraction of water samples. The nanofibrous structure of

272   electrospun PET increased the hydrophilicity of the surface area and provided more paths for

273   diffusion of analyte through the fibrous polymeric matrix, and thus facilitated better interaction

274   between the adsorbent and Cr(VI)-diphenylcarbazide. The selectivity and sensitivity of the

275   method were improved with adding 1,5-diphenylcarbazide as complexing agent for Cr(VI), and

276   sodium dodecyl sulfate (SDS) as surfactant. The adsorption and desorption conditions were

277   studied and optimized with one-at-a-time methodology. In comparison to the previously reported

278   methods the proposed method benefits the advantages of lower LOD, a relatively wide LDR,

279   high enrichment factor, low volume of sample solution, and low volume of a nontoxic desorption

280   solvent (EtOH).

281

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429   *Figure captions*

430   **Fig. 1.** Scheme of electrospinning set up.

431   **Fig. 2.** The SEM micrographs of the electrospun polyethylene terephthalate (PET).

432   **Fig. 3.** Effect of desorption solvent type, volume, and time. Conditions: DPC, 6×10^{-5} mol L^{-1};

433   SDS, 5 mg; pH, 1.7; adsorbent, 5 mg; and adsorption time, 20 min.

434   **Fig. 4.** Effect of pH, and DPC concentration. Conditions: desorption solvent, EtOH (200 μL);

435   SDS, 5mg; adsorbent, 4 mg; adsorption time, 20 min; and desorption time, 5 min.

436   **Fig. 5.** Effect of SDS, and adsorbent dosage. Conditions: desorption solvent, EtOH (200 μL);

437   DPC, 6×10^{-5} mol L^{-1}; pH, 1.7; adsorption time, 20 min; and desorption time, 5 min.

438   **Fig. 6.** Effect of salt, and adsorption time (stirring time).Conditions: desorption solvent, EtOH

439   (200 μL); DPC, 6×10^{-5} mol L^{-1}; SDS, 5 mg; pH, 1.7; adsorbent dosage, 5 mg; and

440   desorption time, 5 min.
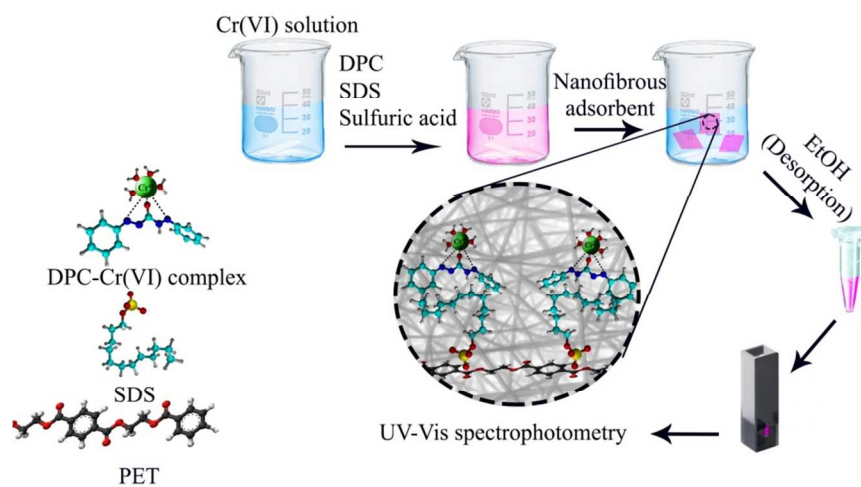
The SPME method based on electrospun PET nanofibers coupled with UV-Vis spectrophotometry for detection of Cr(VI) in water.
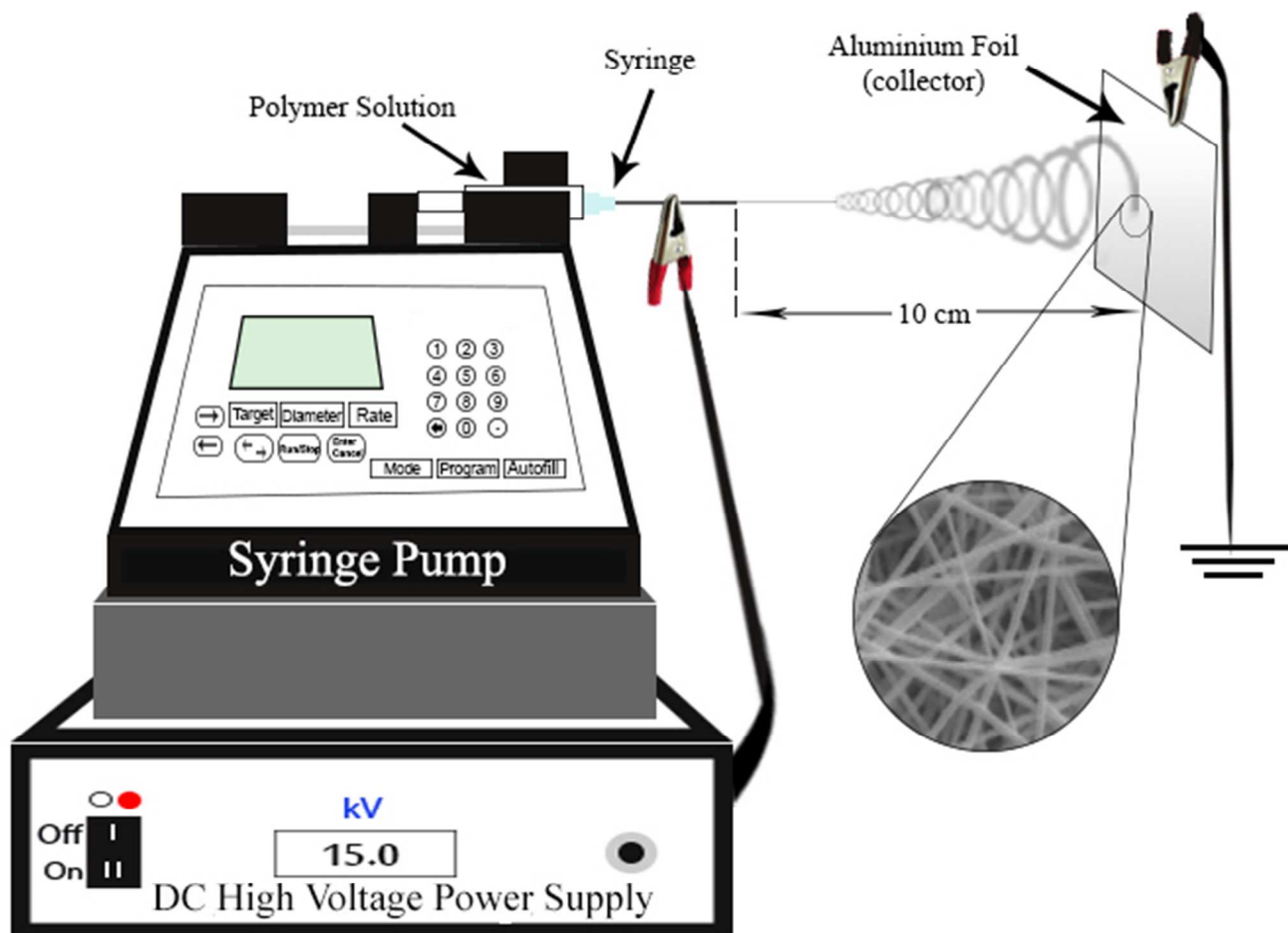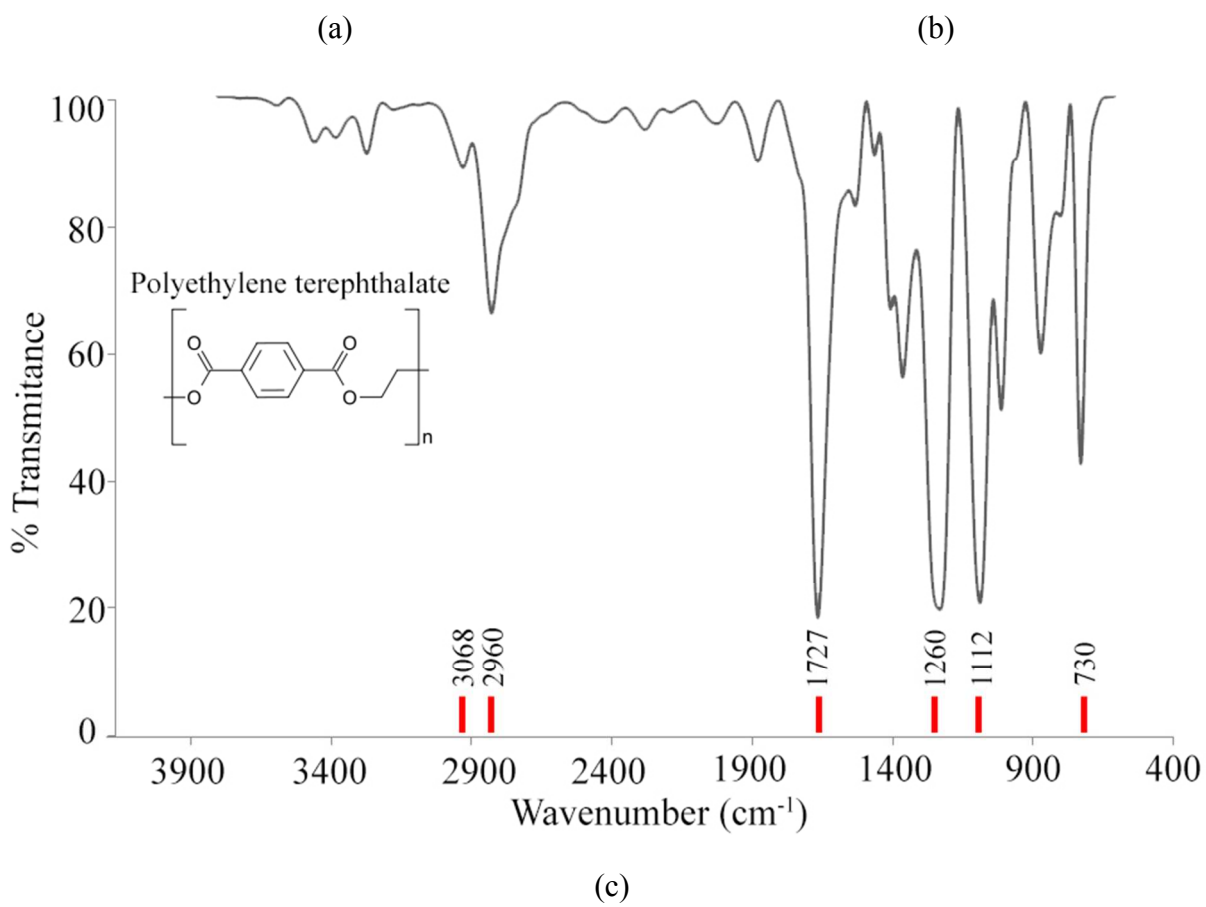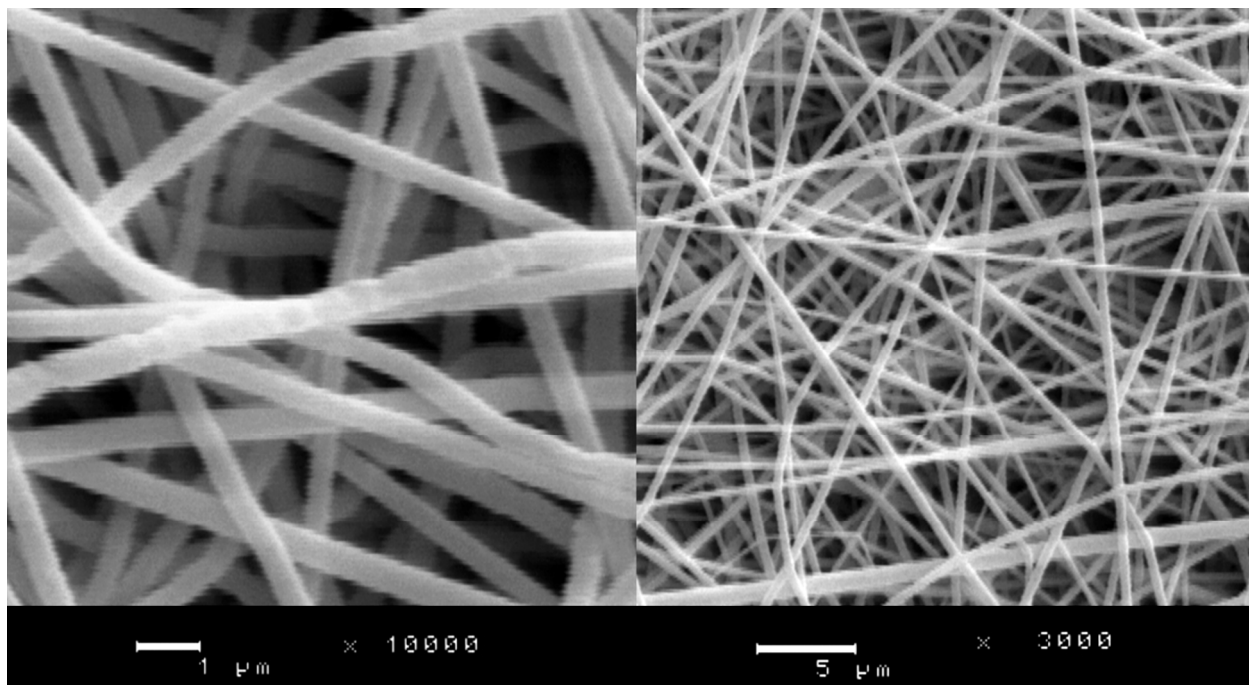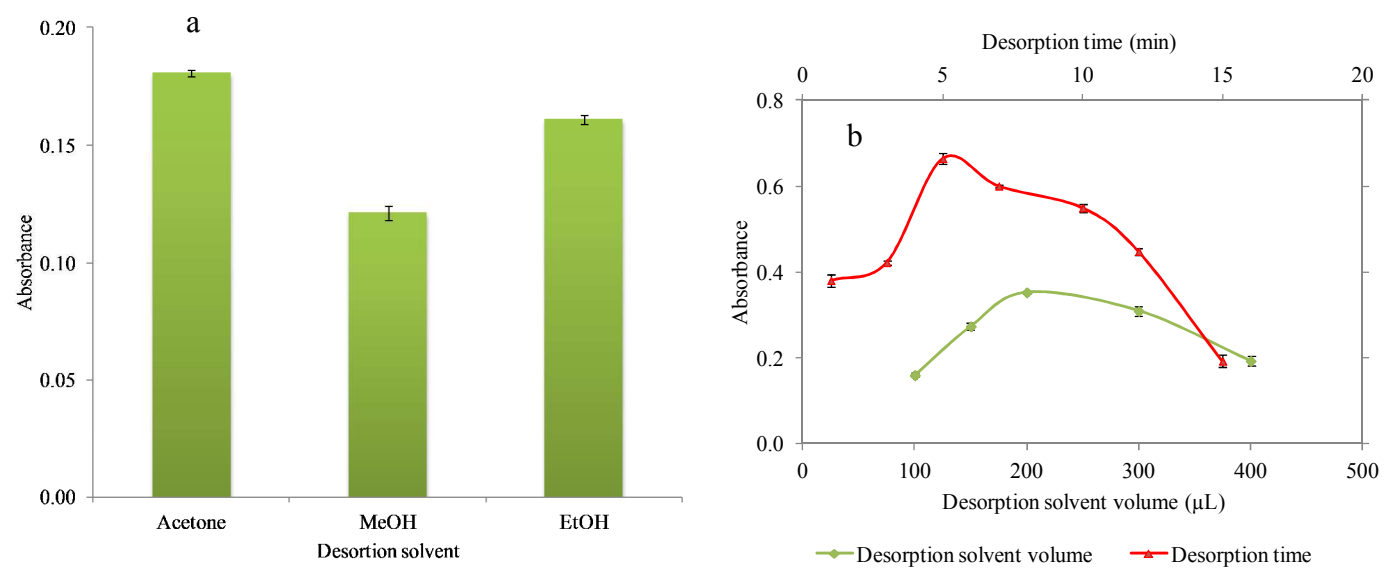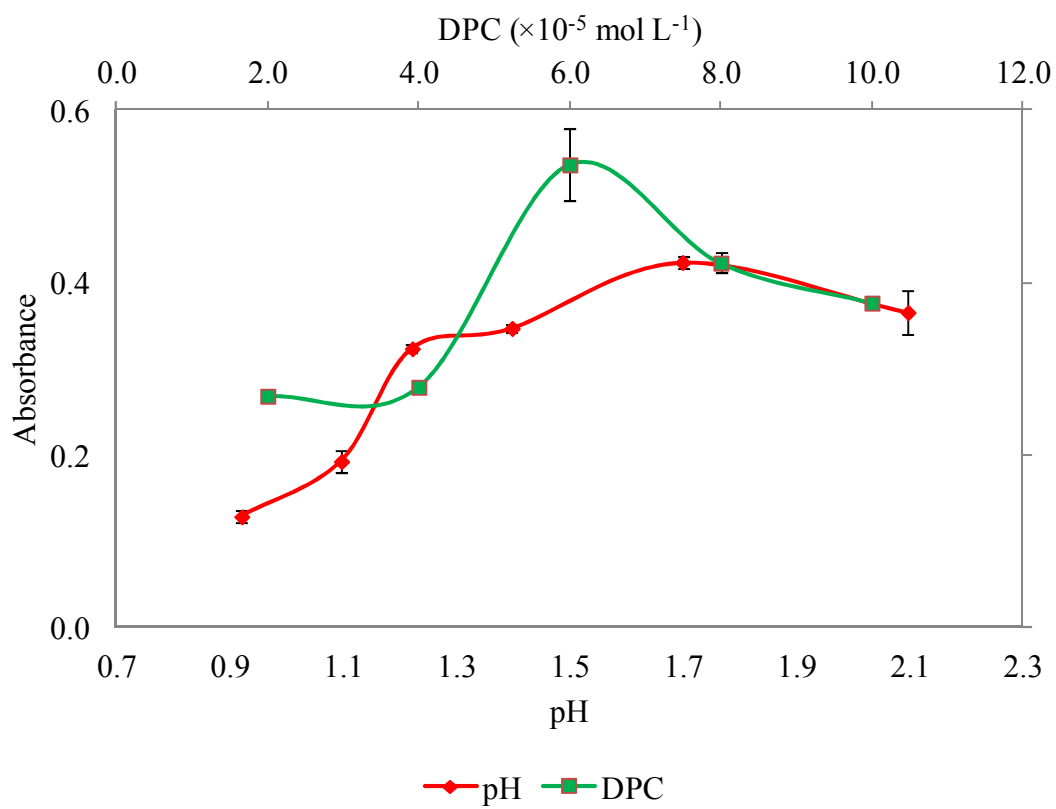
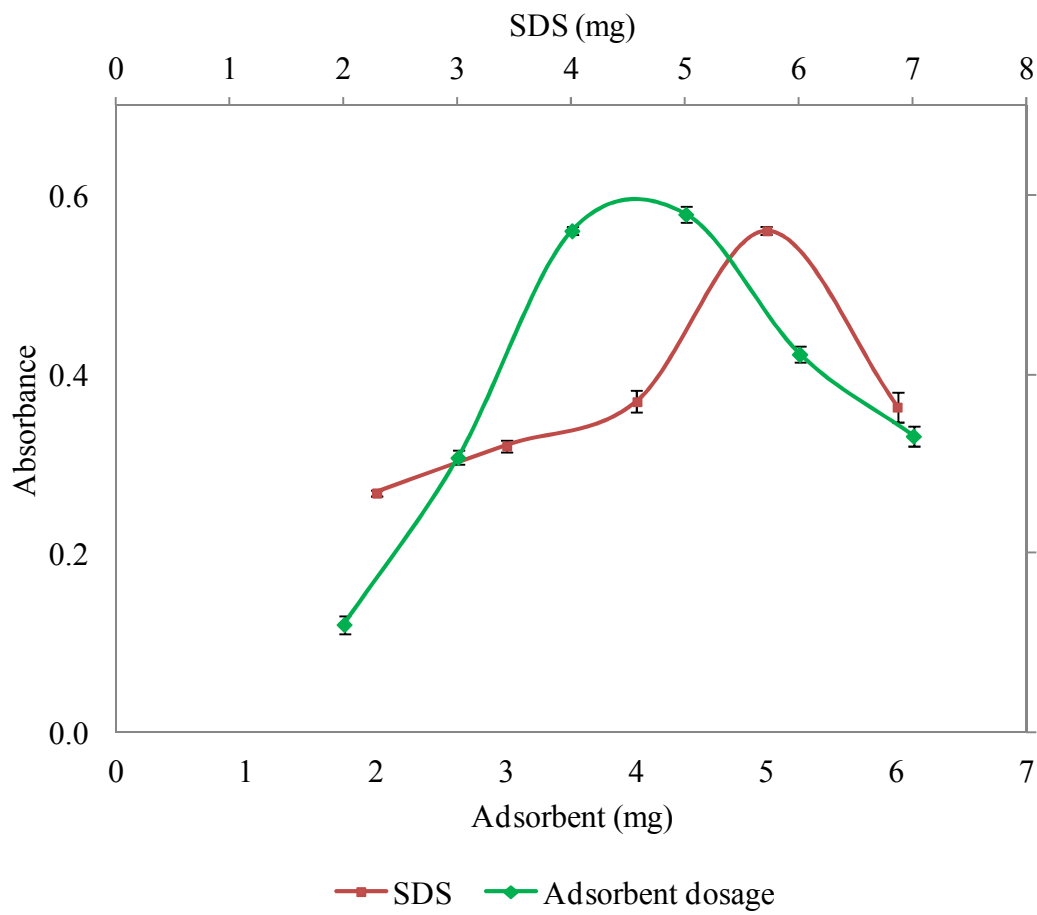Fig. 1

(a)   (b)

(c)

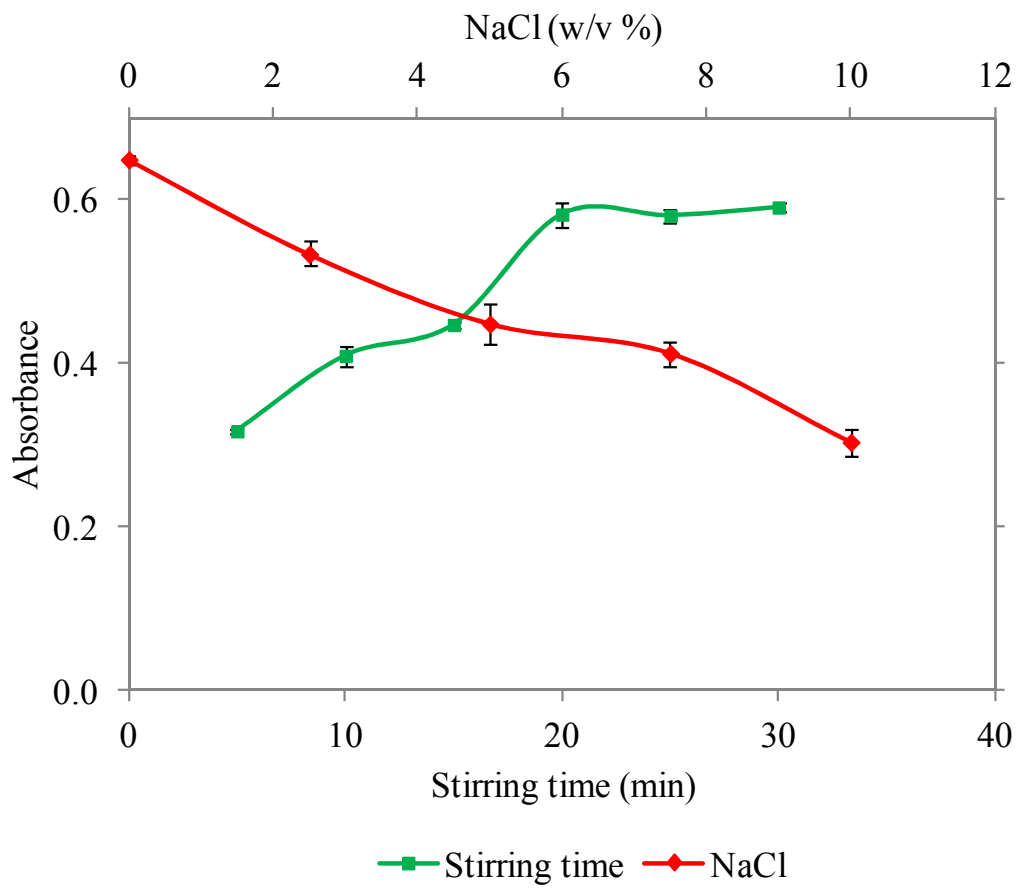Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Table 1. Effect of potential interfering ions on the determination of 25ngmL^{-1} chromium(VI) solution.

Interfering ions	Interfering ion to Cr (VI) ratio (w/w)	RR^a (%) ± SD
Hg^{2+}	50	97.8 ± 1
VO_3^-	50	98.3 ± 2
MoO_4^{2-}	100	99.2 ± 1
Cu^{2+}	10000	98.4 ± 1
NO_3^-	10000	99.1 ± 2
PO_4^{3-}	10000	98.7 ± 3
SO_4^{2-}	10000	99.5 ± 1
Fe^{3+}	10000	98.4 ± 2

^{a}Relative recovery

Table 2. Analytical results for chromium (VI) in real samples.

Sample	Added (ng mL^{-1})	Founded (ng mL^{-1})	RSD[a] (%)	RR[b] (%)
	0	-	-	-
Zayandeh-rud river[c]	10	9.9	1.2	99
	40	38.8	1.3	97
	0	-	-	-
Tap water[d]	10	9.76	1.1	97.6
	40	38.9	1.4	97.2
	0	-	-	-
Ground water[e]	10	9.91	1.3	99.1
	40	39.1	1.6	97.8
	0	-	-	-
Sewage [f]	10	9.85	1.2	98.5
	40	38.76	1.5	96.9

[a]Relative standard deviation (n=3). [b]Relative recovery. [c]Isfahan city, Iran. [d] Tap water was taken from our laboratory (Tehran, Iran). [e&f]Karaj city, Alborz province, North of Iran.

Table 3. A comparison of the proposed method with other reported studies for determination of Cr(VI).

Adsorbent	Detection method	Desorption solvent (mL)	Application	Sample (mL)	EF [a]	Time (min)	LOD [b]	LDR [c]	RR (%)	RSD (%)	Ref. [d]
TRG[e] modified SiO$_2$ composite	UV-Vis.	EtOH,0.15	Tap, sewage,ground and river water	25	166.6	17	0.4	1.3-40	92.6-109.9	2.3	42
Amberlite XAD-16	FAAS[f]	MeOH/H$_2$SO$_4$,10	Tap water	250	25	> 72	45	45-2000	99.4	1	43
Chitin	UV-Vis.	MeOH/CH$_3$COOH, 1	Natural water	100	100	15	50	50-600	98-105	1.7	44
C$_{18}$	UV-Vis.	MeOH, 2	Drinking water	50	25	10	3	0-500	96.1-102	3.4	45
Alumina	UV-Vis.	MeOH, 10	Electroplating wastewater	250	25	> 55	5	0-500	98-98.7	5	46
Ambersorb 563	UV-Vis.	Acetone, 5	Wastewater	150	30	> 75	3.4	-	100-104	<6	47
AAM[g]-silica gel	UV-Vis.	PEG[h]/H$_2$SO$_4$, 10	Electroplating wastewater	250	25	> 62	6	0-1000	97-99	3.5	48
Naphthalene	FAAS	DMF[i],10	Tannery effluents	1000	100	>15	0.5	0-200	-	3.1	49
SDS-coated alumina	UV-Vis.	Acetone/ MeOH/HCl, 8	Tap water	800	100	>30	0.033	-	98-102	3.4	50
Amberlite XAD-1180	FAAS	HNO$_3$/Acetone, 2	Wastewater	150	75	>40	7.7	-	96-104	5.1	51
Electrospun PET	UV-Vis.	EtOH, 0.2	Tap, sewage, ground and river water	25	125	25	0.6	1.8-60	96.9-99.1	1.6	This work

[a] Enrichment factor. [b] Limit of detection (ng mL^{-1}). [c] Linear dynamic range (ng mL^{-1}). [d] Reference. [e] Thermally reduced graphene. [f] Flame atomic absorption spectroscopy. [g] Acid activated montmorillonite. [g] Polyethylene glycol. [i] Dimethyl formamide.