On-Line Separation and Determination of Trivalent and Hexavalent Chromium with a New Liquid Membrane Annular Contactor Coupled to Inductively Coupled Plasma Optical Emission Spectrometry

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Abstract: We describe a new on-line sensitive and selective procedure for the determination of trivalent and hexavalent chromium in liquid samples by a tailor-made contactor (TMC), specifically a liquid membrane annular TMC, coupled with inductively coupled plasma with optical detection. The TMC was designed and developed to integrate the extraction and stripping phases of the analyte in one module to minimize the membrane solvent's consumption and maximize the speed of transport through the liquid membrane. Moreover, the particular geometry studied, which consists of two coaxial hollow fibers, allows the TMC to be used for both separating and preconcentrating purposes. Both (−)-N-dodecyl-N-methylephedrinium bromide (30 mM) in dichloroethane and HNO$_3$ (0.75 M) were used as the liquid membrane and receiving solution, respectively. The proposed method's performance was evaluated in terms of the hexavalent chromium extraction efficiency and the coefficient of variation percentages; these were higher than 85% and less than 5%, respectively. In addition, the proposed procedure was applied to two real samples: a tap water sample and an eluate from solid urban waste. In both cases, the analytical performances were good and comparable to those obtained using synthetic standard solutions.

Keywords: toxic element; speciation analysis; liquid membrane; hollow fibers; pertraction

1. Introduction

Chromium (Cr) has a wide range of applications, for example, in stainless steel industries; in several chemical industries for the production of pigments, explosives, ceramics, anticorrosive and antiseptic products; and in the galvanic and tanning industries [1–3]. This intensive use of Cr has led to a considerable release of the element into the environment, often as waste [4,5]. Although Cr may exist in several states of oxidation, trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] are the two most stable oxidation states, and they have different toxicities, mobilities, and bioavailabilities [6,7]. While Cr(III) is characterized by low toxicity and is considered an essential nutrient in the metabolism of glucose, protein, and fat [8–10], Cr(VI) is well known to be highly toxic. It is classified as a carcinogen possessing mutagenic and teratogenic properties [10,11].

The determination of the total chromium (Cr$_{TOT}$) concentration is not a good indication of the real impact on the environment and human health. Therefore, it is necessary

to use sensitive and selective analytical techniques that can separate and measure the two species even at very low concentrations on the order of µg/L. Due to their different environmental behavior, the regulations require, in certain cases, different limits for the two chemical forms. In Europe, the legal limits for Cr_{TOT} and Cr(VI) in groundwater or drinking water are 50 and 5 µg/L or 50 and 10 µg/L, respectively [12–14]. In recent years, scientific interest in the optimization of analytical methods for the differentiation between Cr(III) and Cr(VI) has increased [15–32]. The most common off-line methods consist of separation steps and preconcentration (by ion exchange columns, liquid–liquid, solid phase extraction (SPE), high-performance liquid chromatography (HPLC)), followed by flame atomic absorption spectrometry (F-AAS) [16–19], graphite furnace atomic absorption spectrometry (GF-AAS) [20–22], electrothermal atomic absorption spectrophotometry (ET-AAS) [23,24], voltammetry [25,26], inductively coupled plasma optical emission spectrometry (ICP-OES) [27–30] or mass spectrometry (ICP-MS) [31–33]. An on-line method such as a fiber-packed column coupled to F-AAS [34], a flow-injection system, which combines an F-AAS [35] or ET-AAS [36], and on-line preconcentration of Cr species by SPE–HPLC–ICP-MS [37] were also proposed. On-line methods offer various advantages over off-line methods; the direct coupling of separation and detection systems allows for low sample handling, which reduces the likelihood of contamination, and allows also for fast separation, identification, and quantification of the analytes. The main drawbacks of the above methods are a high cost of analysis and, in the case of chromatographic techniques, the dilution of the species during elution with the consequence of increasing the detection limits. An alternative approach for the redox speciation of elements is the use of contactors based on liquid membrane processes [38–41]. The separation by liquid membranes is based on the use of a solution consisting of an organic solvent and a water-immiscible carrier (membrane solution), which can selectively bind to the species to be transported. This species is then transported from a starting solution (feed) to an arrival solution (receiving) by two exchange processes at the interfaces with a liquid membrane. Liquid membrane processes offer various advantages. There is no change in the element's chemical properties and no need to add any denaturing chemicals. Furthermore, these devices allow the compounds to be both separated and preconcentrated, and the solvent can be regenerated for more efficient and selective separation. There are several configurations for liquid membrane technologies [42]. Among these, the contained liquid membrane systems and the integrated membrane extraction-stripping (pertraction) systems are particularly convenient due to their high stability and flexibility [43–48]. In this technology, the solutions (feed, membrane, and receiving) are divided by porous surfaces, which contain the solutions even under a flow regime while remaining permeable to solutes. Contained liquid membranes typically consist of hollow fibers arranged in two modules; each module is responsible for one step of the overall transport process (either extraction of the chemical species from the feed solution to the membrane or stripping from the membrane to the receiving solution) [49,50]. Several applications for the separation and removal of Cr(VI) have been reported, which involve the use of microporous hollow fiber modules built in different arrangements [51–54]. However, in these devices, the efficiency of transport is strongly influenced by the volume of the solutions and the contact surfaces' width. The major drawback of these systems is the large quantity of membrane solution required, which significantly slows down the overall process due to the discontinuity between the extraction and removal operations. To overcome these disadvantages, our research work focuses on the design and development of a new hollow fiber contactor and its application in the separation of Cr(III)/Cr(VI). This tailor-made contactor (TMC) is able to perform two steps (i.e., extraction and stripping) in a single module in order to reduce the consumption of membrane solvent and maximize the speed of transport. The particular geometry with coaxial fibers also allows for the application of the TMC for both separation and preconcentration purposes. Finally, we optimize and apply the coupling of the TMC to ICP-OES to obtain on-line measurements of Cr(III) and Cr(VI) concentrations.

2. Materials and Methods

2.1. Design and Development of the TMC

The developed TMC is based on hydrophobic hollow fibers in polypropylene (Accurel pp q 3/2 diameter: 1.8 mm; Accurel pp s 6/2 diameter: 0.6 mm) supplied by Membrana-GMBH (Wuppertal, Germany). The smaller fibers were inserted inside the larger ones in order to obtain an annular chamber between the pair of fibers. These couples were then inserted into a glass cylinder and fixed to polytetrafluoroethylene (PTFE) supports. In this way, the feed, membrane, and receiving solutions flow independently through the three confined spaces, and the two processes at the interfaces coexist within a single module. All parts of the TMC are shown in Figure 1. A more detailed description of the TMC assembly is given in the Supplementary Material (Figure S1).
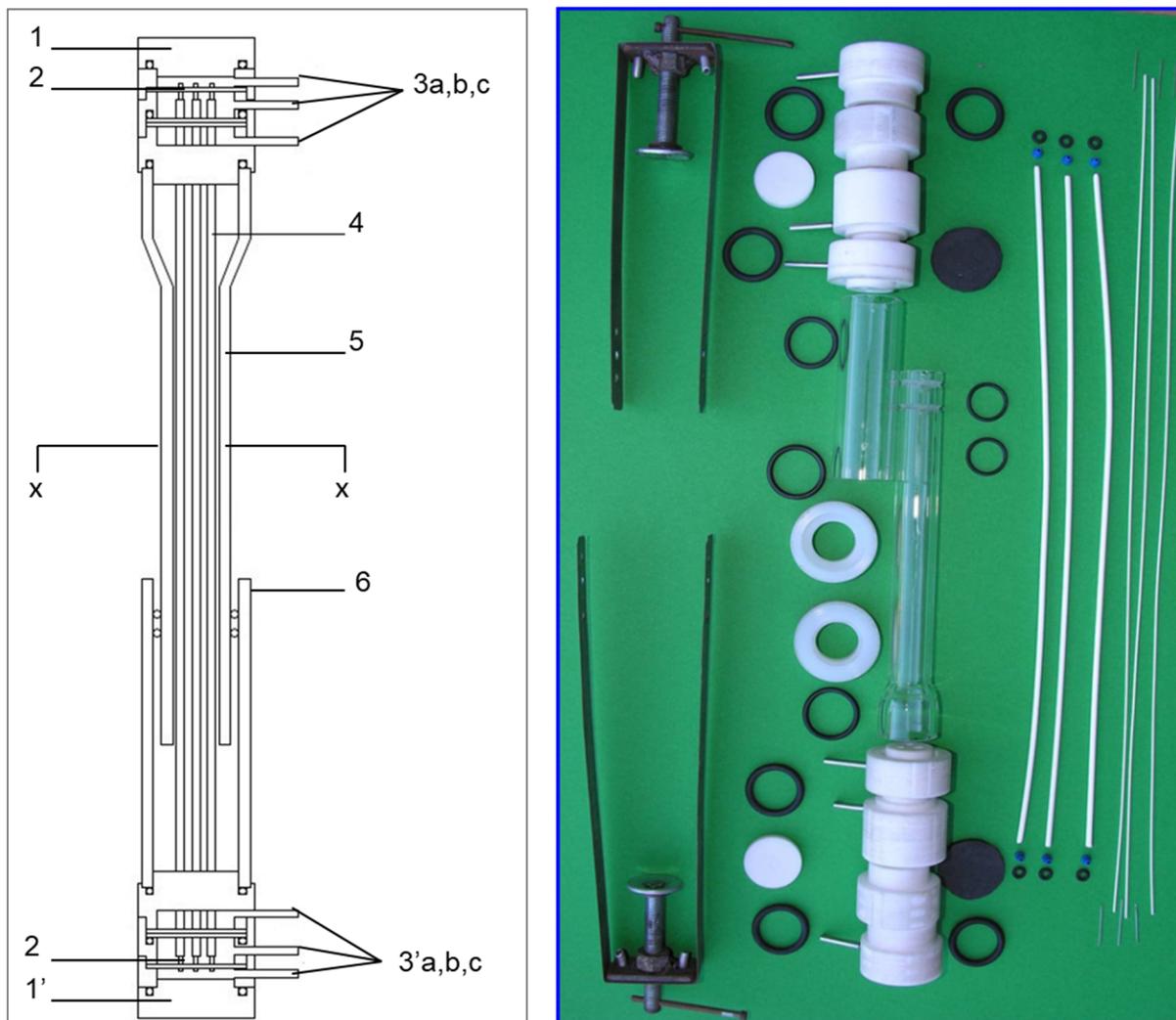
Figure 1. Longitudinal schematic section and parts of the annular contactor. (1, 1′) stopper made of polytetrafluoroethylene (PTFE); (2) first hollow fiber with a smaller diameter; (3a,b,c, 3′a,b,c) threaded spouts (in steel) for the feeding (inlet/outlet) of the feed, receiving and membrane solutions; (4) second hollow fiber with a larger diameter; (5) first cylinder (glass) with a smaller diameter; (6) second cylinder (glass) with a larger diameter.

In the construction of the TMC, we designed and developed two different anchorage systems for small and large fibers (described in the Supplementary Material) to avoid the use of any glues, which are known to be chemically attacked by organic solvents. To change the flow of all the solutions inside the TMC independently, two peristaltic pumps (205S/CA model, Watson-Marlow Inc., Wilmington, MA, USA and Alitea, Medina, WA,

USA) were used. In fact, the flows must be suitably supported both at the input and at the output to prevent high-pressure drops within the TMC and to minimize the pressure differences on the hollow fibers' surfaces. We used PVC grey/grey tubes with a 1.3-mm inner diameter (CPI International, Santa Rosa, CA, USA) for the feed solution, Viton tubes with a 2-mm inner diameter (DuPont, Wilmington, DE, USA) for receiving, as well as membrane solutions. Figure 2 shows the operation of the TMC: The membrane solution flows in the annular space (working area = 8.2 mm^2), while the feed and receiving solutions can alternately flow inside the smaller fibers and outside the larger ones. If the supply of feed and receiving solutions is inverted, the TMC can work in two modes (A and B), characterized by different volume ratios between the feed and the receiving solutions. The TMC in mode A can be used for separation purposes: When the feed solution flows inside the small fibers, the extraction process from the feed solution is promoted, and it is possible to remove the transported chemical species from the feed solution efficiently. On the contrary, when the TMC is in mode B, it can be used for preconcentration purposes because when the receiving solution flows inside the small fibers, the transport from the feed to the receiving solution tends to concentrate the analyte in the receiving solution. In fact, with the addition of suitable reagents that are able to take the permeate away continuously; a condition of counter gradient transport is quickly achieved with a thermodynamically favorable transmembrane transport. In this way, it is possible to have both separation and enrichment in the extracted species' concentration in the receiving solution. The employed annular geometry allows the ratio between the membrane volume (reduced to a minimum) and the exchange surface at the feed/membrane and membrane/receiving interfaces to be optimized. This allows the rate of transmembrane transport to be increased while the consumption of organic solvents is reduced. It is evident that the TMC is extremely versatile because it allows the volume ratios to be varied and the solutions can flow both in cocurrent and in countercurrent. In our device, the minimum solution volumes, which include dead volumes at the upper and lower ends of the contactor and inside the peristaltic tube, were 10 mL for solutions flowing into the inner fibers (feed or receiving) and annular space (membrane) and 250 mL for solution flowing outside the fibers.
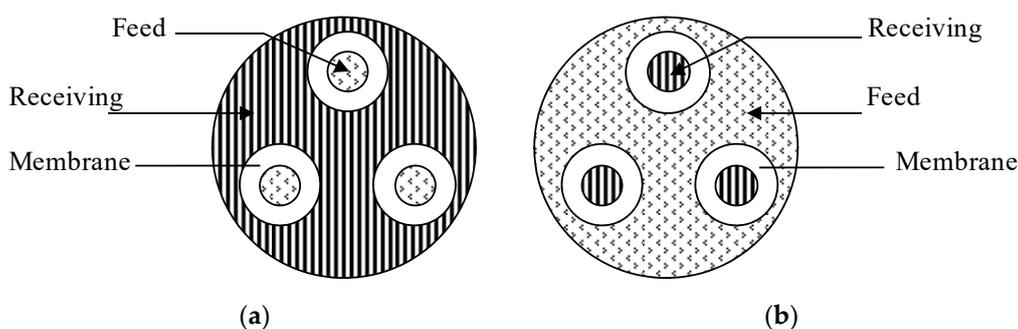
Figure 2. Tailor-made liquid membrane annular contactor operating modes: (**a**) mode A for separation purposes: feed inside small fibers and receiving outside of large fibers; (**b**) mode B for preconcentration purposes: receiving inside small fibers and feed outside of large fibers.

2.2. Analytical Determination

The Cr(VI) concentration was determined with 1,5-diphenylcarbazide (Sigma-Aldrich, Merck KGaA, Darmstadt, Germany) by a UV–visible spectrophotometer at 540 nm (Cary 50, Agilent Technologies, Santa Clara, CA, USA) according to the standard methods [55]. Briefly, before the spectrophotometric analysis, 0.2 mL 1,5-diphenylcarbazide solution and 0.1 mL H_2SO_4 (1:1) (Carlo Erba Reagents, Milan, Italy) were added to 10 mL of the sample solution. Deionized H_2O (resistivity, 18.2 MΩ cm) from a Purelab Plus system (Elga LabWater NA, Woodridge, IL, USA) was used throughout the study. The Cr_{TOT} concentration was determined by an ICP-OES (Varian Vista MPX, Mulgrave, Australia)

equipped with an ultrasonic nebulizer (Cetac Technologies U 5000 AT+, Omaha, NB, USA). The ICP-OES reading parameters in the off-line and on-line modes are shown in Table 1. In all solutions, beryllium (Be) was added as an internal standard at a concentration of 0.2 mg/L, which was obtained by dilution with deionized water of a certified standard at 1001 ± 8 mg/L (Merck KGaA, Darmstadt, Germany). The external calibration was performed with three solutions at known concentrations (0.025, 0.05, and 0.1 mg/L) obtained by dilution of certified standards at a Cr concentration of 1000 ± 3 mg/L (Exaxol Italia Chemical Manufactories s.r.l., Genoa, Italy). The analytical line was 267.716 nm, and the alternative analytical lines were 206.158 and 284.984 nm.

Table 1. ICP-OES reading parameters.

Parameters	Off-Line Mode	On-Line Mode
Plasma gas flow (L/min)	16.5	16.5
Auxiliary gas flow (L/min)	1.50	1.50
RF Power (kW)	1.30	1.30
Nebulizer pressure (KPa)	230	230
Rinse time (s)	15	0
Instrument stabilization delay (s)	45	0
Replicate read time (s)	30	20
Number of replicates	3	5
Pump rate (rpm)	20	5

2.3. Selection of Carrier, Membrane Solvent, and Receiving Solution

To obtain a suitable facilitated transport system of Cr(VI), it was necessary to select a carrier that was soluble in the membrane solvent and able to selectively form adducts with Cr(VI) (K_2CrO_4, RPE-ACS, Carlo Erba, Milan, Italy). The transport from the membrane solution to the receiving solution has to be complemented by a countertransport mechanism, which involves the exchange between Cr(VI) and another anion that replaces it in the ionic pair formation. In order to make the reaction thermodynamically favored, a strong acid (HA) was used in the receiving solution; in this way, the anion (A^-) guarantees the countertransport, and the acidity (H_3O^+) allows for the subtraction of chromate at equilibrium by protonation. Given these considerations, we carried out several batch experimental tests to choose the carrier, the solvent membrane, and the receiving solution for our system. To obtain an efficient transport of Cr(VI), it is necessary that Cr(VI) and Cr(III) are barely soluble in the solvent membrane to avoid nonfacilitated transport, i.e., to avoid transport without a carrier, which would decrease the selectivity. Furthermore, the carrier must be selective for Cr(VI), soluble in the solvent membrane but not soluble in water, and the receiving solution has to maintain the thermodynamically favored release of Cr(VI) from the membrane (the extraction equilibrium at the membrane/receiving interface must be sufficiently shifted to the receiving solution). Kerosene [51,53], dichloromethane [56,57], and 1,2-dichloroethane [58] (RPE-ACS, Carlo Erba, Milan, Italy) were tried as membrane solvents. Aliquat 336 (Sigma-Aldrich, Steinheim, Germany) [52,59] and (−)-N-Dodecyl-N-methylephedrinium bromide [(−)-DMEB] [60] (99%, Sigma-Aldrich, Steinheim, Germany) were tested as carriers at a concentration of 5, 10, 30, and 100 mM. HNO_3 [52,61] (65% RPE, Carlo Erba, Milan, Italy) and HCl [62] (37% RPE, Carlo Erba, Milan, Italy) were tested as receiving solutions in the concentration range from 0.3 to 1.5 M. Ultimately, 1,2-dichloroethane was selected as a membrane solvent because it does not ruin the TMC parts and simultaneously provides good carrier solubilization and poor Cr(VI) solubility. Regarding the receiving solution, HNO_3 was chosen because the transport speed of Cr(VI) was higher than that in the presence of HCl. In particular, the maximum rate of extraction was achieved at a concentration of HNO_3 equal to 0.75 M, according to that reported in the literature for Aliquat 336 [63]. Therefore, the following analyses were carried out at this concentration. Finally, (−)-DMEB was chosen as the carrier because it reduces the accumulation of Cr(VI) in the membrane solution and is barely hygroscopic, such that it

does not need many precautions in the weighing phase, in comparison with Aliquat 336, which, on the other hand, is highly viscous and hygroscopic. Lastly, (−)-DMEB was used at a concentration of 30 mM, as it allowed for an effective extraction of the feed/membrane interface without preventing the release of the membrane/receiving interface. All tests were repeated in triplicate.

3. Results and Discussion

3.1. TMC Performance for Cr(VI) Transport

The optimized transport system was evaluated in terms of the mass distribution of Cr(VI) among the three phases (feed, membrane, receiving) involved in the exchange process (Figure 3).
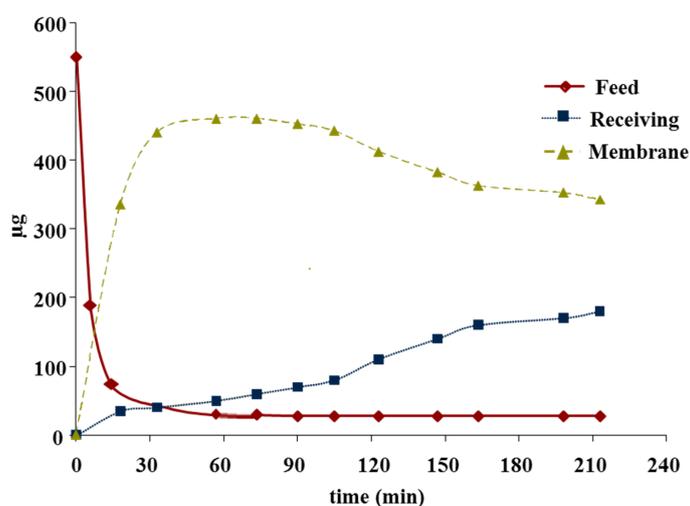
Figure 3. Distribution of Cr(VI) in the feed, membrane, and receiving solutions set on recirculation. Carrier, [(−)-DMEB] = 30 mM, membrane solution volume = 50 mL; feed, [Cr(VI)] = 10 mg/L, feed solution volume = 55 mL; receiving, [HNO$_3$] = 0.75 M, receiving solution volume = 250 mL.

For these tests, all solutions were set on recirculation, and the feed solution was passed into the small fibers (Figure 2a). The feed and receiving solutions, which were sampled every 30 min, were analyzed off-line. The membrane solution concentrations were calculated as the difference between the volumes and feed and receiving concentrations. After the first phase (15 min), the equilibrium predominantly involves the feed/membrane interface. While the Cr(VI) is extracted from the feed solution, the membrane is loaded with Cr(VI) and slowly released to the receiving solution. Moreover, it can be noticed that the transport process from the feed to the receiving solution continues to occur even when the concentration of Cr(VI) in the receiving solution becomes higher than the concentration of Cr(VI) in the feed solution. This is possible thanks to the presence of an excess HNO$_3$ in the receiving solution that maintains the transport process's driving force. The transport conditions ensure that the TMC operates correctly in removing Cr(VI) over long periods without any variation in the removal efficiency. This result was confirmed by experimental trials carried out under conditions that facilitate the achievement of membrane saturation. The feed solution was passed outside the hollow fibers (Figure 2b), continuing to supply the system with a Cr(VI) solution at a concentration of 10 mg/L. The receiving solution, which flows inside the small fibers, was instead set on recirculation, trying to minimize its total volume (10 mL) to obtain a faster preconcentration. Under these conditions, the Cr(VI) extraction at the feed/membrane interface is favored by both the high contact surface and the analyte's continuous supply. At the same time, the transport to the receiving solution is disadvantaged because of the increasing accumulation of the analyte in the receiving solution. In Figure 4, the measured Cr(VI) concentrations in the feed and receiving solutions at the device's outlet are reported. It is worth noting that at the beginning, a very

low Cr(VI) concentration was observed in the receiving solution, since 15 min was the time needed to achieve pseudostationary conditions. After this time, the concentration of Cr(VI) in the receiving solution begins to increase almost linearly, with constant transport efficiency, even under the conditions of countergradient concentration. After 30 min, the receiving solution's concentration becomes approximately equal to the residual in the feed solution. At this point, Cr(VI) begins to be transported from the solution at a lower concentration (feed) to the solution at a higher concentration (receiving), with no reduction in the transport speed rate. After 2 h of operation, the concentration in the receiving solution is higher than that of the feed solution at the inlet of the TMC ([Cr(VI)] = 10 mg/L). It is interesting to note that the transport process from the feed to the receiving continues to take place even when the concentration in the receiving becomes greater than the concentration in the feed solution. This is possible due to an excess of HNO_3 in the receiving and the maintenance of the driving force of the transport process. This feature, as mentioned above, is particularly interesting for another possible application, namely as a system for the analyte preconcentration.
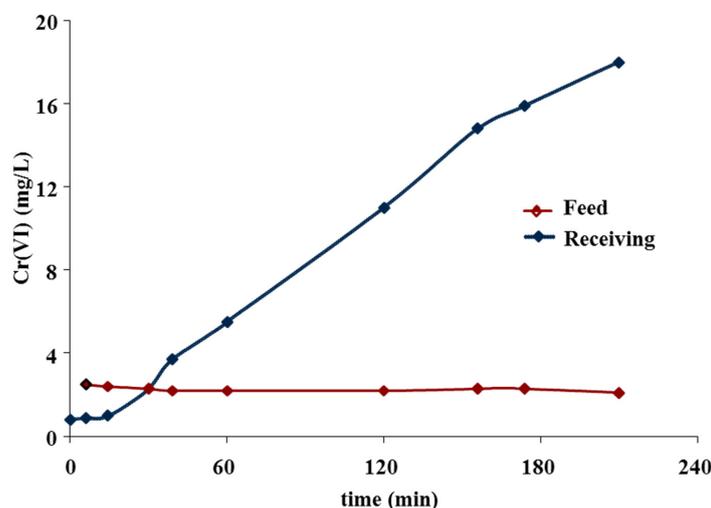
Figure 4. Variation in the Cr(VI) concentration (mg/L) in the feed solution (in continuous supply) and the receiving solution (in recirculation, 10 mL) at the outlet of the contactor. Membrane [(−)-DMEB] = 30 mM, membrane solution volume = 50 mL; [Cr(VI)] = 2.5 mg/L; receiving $[HNO_3]$ = 0.75 M.

Cr recovery tests (TMC in mode A; Figure 2) were carried out, maintaining membrane and receiving solutions on recirculation. Since the flow rate and the concentration of the feed solution can influence the removal efficiency of Cr(VI), the variation in the extraction efficiency percentage (E%), that is, the recovery of Cr obtained from the extraction and stripping step arranged in a single module, was evaluated using the following formula:

$$E\% = \frac{[Cr(VI)]in - [Cr(VI)]out}{[Cr(VI)]in} \times 100 \tag{1}$$

where [Cr(VI)]in is the Cr(VI) concentration in the starting solution and [Cr(VI)]out is the Cr(VI) concentration at the outlet of the TMC.

On examining the E% (Table 2), an almost quantitative yield can be noted for flow rates less than or equal to 0.30 mL/min. This rate was selected for the following coupling of the TMC with the ICP-OES. The E% of Cr(VI) as a function of the concentration in the feed solution entering the contactor was studied for a Cr(VI) concentration ranging from 3 to 100 µg/L (Table 2). The TMC is able to operate with a good E% even in the range of Cr(VI) concentrations typical of several common environmental matrices ranging from less than 5 µg/L up to more than 50 µg/L (ground waters [64], lake waters [19], tap water [65,66], wastewater [19,67,68]). Before the validation of the method on mixtures containing both

forms of Cr, as for Cr(VI), the removal efficiency of Cr(III) was evaluated by varying its concentration in the feed solutions entering the device. The range of concentrations explored was very wide (20–5000 µg/L). It was observed that, regardless of its input concentration, the Cr(III) concentration was not significantly changed during the passage inside the contactor.

Table 2. The extraction efficiency percentage (E%) on varying the Cr(III) and Cr(VI) concentrations and the flow rate (mL/min) of the TMC in mode A (feed inside small fibers and receiving outside of large fibers), with membrane and receiving solutions on recirculation.

[Cr(III)] (µg/L)	[Cr(VI)] (µg/L)	Flow Rate (mL/min)	E%
E% of Cr(VI) in function of the peristaltic pump flow rate			
0.0	63.5	0.20	97.1 ± 0.3
0.0	63.5	0.25	95.8 ± 0.7
0.0	63.5	0.30	92.3 ± 0.7
0.0	63.5	0.40	88.1 ± 0.9
0.0	63.5	0.50	86.3 ± 1.1
0.0	63.5	0.70	74.9 ± 1.3
E% of Cr(VI) as a function of the concentration in the feed solution entering the contactor			
0.0	3.0	0.30	85.6 ± 0.9
0.0	5.0	0.30	90.3 ± 0.7
0.0	10.0	0.30	95.8 ± 0.2
0.0	15.0	0.30	96.3 ± 0.4
0.0	50.0	0.30	97.7 ± 0.5
0.0	100.0	0.30	96.7 ± 0.2
E% of Cr(VI) as a function of the Cr(VI)/Cr(III) ratio			
20.0	5.0	0.30	78.2 ± 0.8
20.0	10.0	0.30	85.9 ± 0.9
20.0	20.0	0.30	88.3 ± 0.6
20.0	30.0	0.30	92.5 ± 0.3
20.0	60.0	0.30	95.1 ± 0.3

To evaluate the selectivity of the transport, standard mixtures of Cr(III) and Cr(VI) in different concentration ratios were used. The variation in the E%, that is, the recovery of Cr obtained from the extraction and stripping step arranged in a single module, was evaluated using the following formula:

$$E\% = \frac{[Cr_{TOT}-Cr(III)]in-[Cr_{TOT}-Cr(III)]out}{[Cr_{TOT}-Cr(III)]in} \times 100 \tag{2}$$

where $[Cr_{TOT}-Cr(III)]in$ is the Cr(VI) concentration in the starting solution and $[Cr_{TOT}-Cr(III)]out$ is the Cr(VI) concentration at the outlet of the TMC. Cr_{TOT}, both at the input and at the output, was determined experimentally, while the concentration of Cr(III)in was known and corresponded to the starting solution concentration. The percentage recovery (R%) values of the two forms were then calculated as a percentage ratio between the measured and known concentrations. The results obtained are shown in Figure S2. The TMC still exhibits good performance in the presence of Cr(III) (20 µg/L) and at low Cr(VI) concentrations (5 µg/L), even though in these conditions, a small loss of the system's efficiency was observed (R% < 80%). These results indicate that the contactor can be used to measure the two chemical forms of Cr at levels that are more than acceptable for use in most measures of environmental interest.

3.2. Coupling of the TMC with ICP-OES and On-Line Determination of Cr(III) and Cr(VI)

The TMC was interfaced with the ICP-OES (Figure 5) to realize a system that is able to measure Cr(III) and Cr(VI) in a semiautomatic mode and through a sequential reading

of Cr_{TOT} at the inlet and outlet of the TMC. The coupling was realized by connecting the output of the lower diameter fibers of the TMC directly to the ultrasonic nebulization system of the ICP-OES and using a peristaltic pump set at 0.30 mL/min. A second peristaltic pump with a flow rate of 2.1 mL/min was used to circulate the receiving solution outside the hollow fibers. To carry out sequential measurements of the solution at the input and output of the TMC, a 4-way valve was used, which is shown in Figure 5.
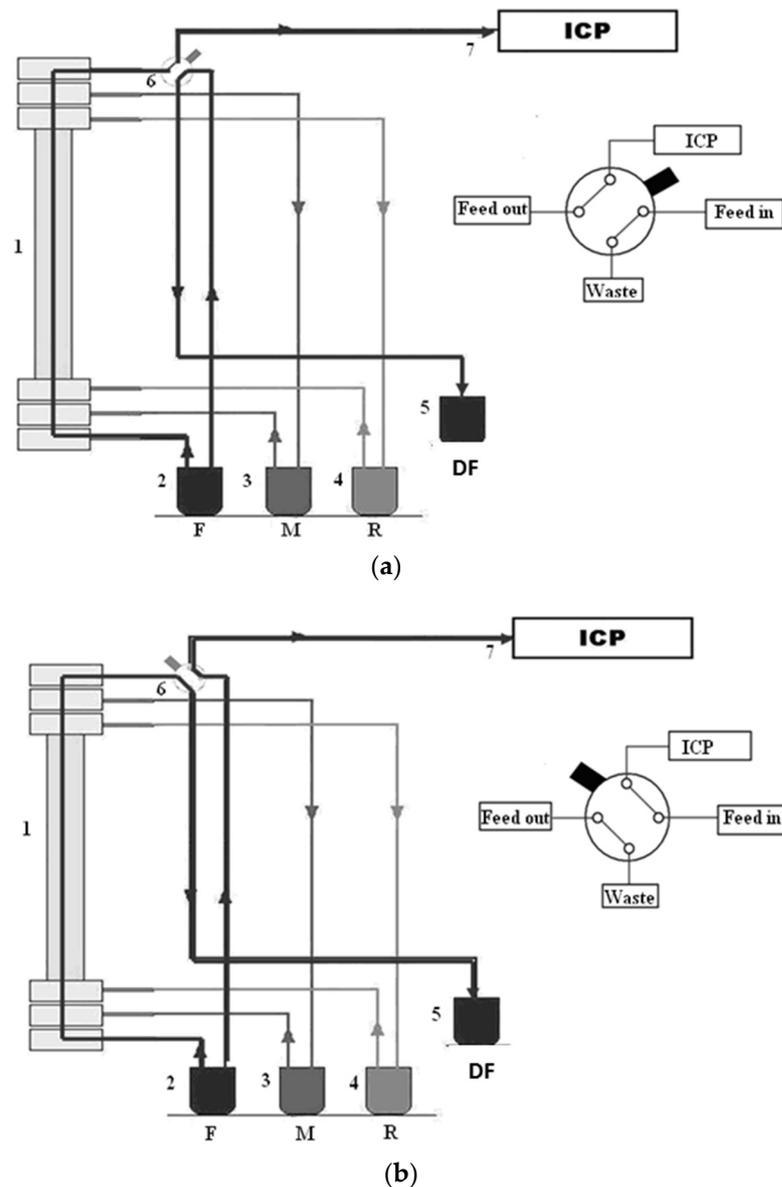
Figure 5. Scheme of the TMC/ICP-OES (tailor-made contactor/inductively coupled plasma optical emission spectrometry) instrumental equipment for Cr(III) and Cr(VI) on-line analysis. In panel (**a**), the solution at the output of the contactor (feed out) arrives at the ICP-OES; in panel (**b**), the solution at the input of the contactor (feed in) reaches the ICP-OES. (1) Contactor; (2) feed solution (F); (3) membrane solution (M); (4) receiving solution (R); (5) drain feed solution (DF); (6) valve; (7) ICP-OES.

When the valve is in the position shown for panel a (Figure 5), the solution at the output of the TMC goes to the ICP-OES, while the solution at the inlet goes to the drain. Since the passage inside the TMC removes Cr(VI), the solution's concentration at the output of the TMC will consist of Cr(III) only. When the valve is in the position shown for panel b (Figure 5), the solution at the output of the TMC goes to the discharge, while the inlet

solution goes directly to the ICP-OES to be analyzed. In this way, Cr_{TOT} is determined, and the Cr(VI) concentration is obtained by the difference.

Optimization of the Quantification Procedure

Before applying the system, the operating conditions that allow for the best analytical performance of the method are needed. The optimization of the ICP-OES operating conditions is concerned particularly with the flow rate at the inlet of the nebulizer and the replicate read time of the detector charged coupled device, which are the parameters that most influence the signal-to-noise ratio. In setting the TMC flow rate to 0.30 mL/min, the peristaltic pump that supports the flow of the feed solution was adjusted at 5 revolutions per minute (rpm). Be was mixed into the flowing feed solution by a "y" connection as an internal standard to control and to correct for variations in the signal due to the nebulization efficiency. More information about the optimization of the signal acquisition time is given in Section S2 ("Optimization of the ICP-OES parameters") and Figure S3 of the Supplementary Material. Under the optimal conditions, the limit of detection (LOD) corresponding to a signal-to-noise ratio equal to 10 was as low as 1 µg/L.

Figure 6 shows some examples under different conditions of the acquired signal (S) and the normalized signal for the internal standard (IS).
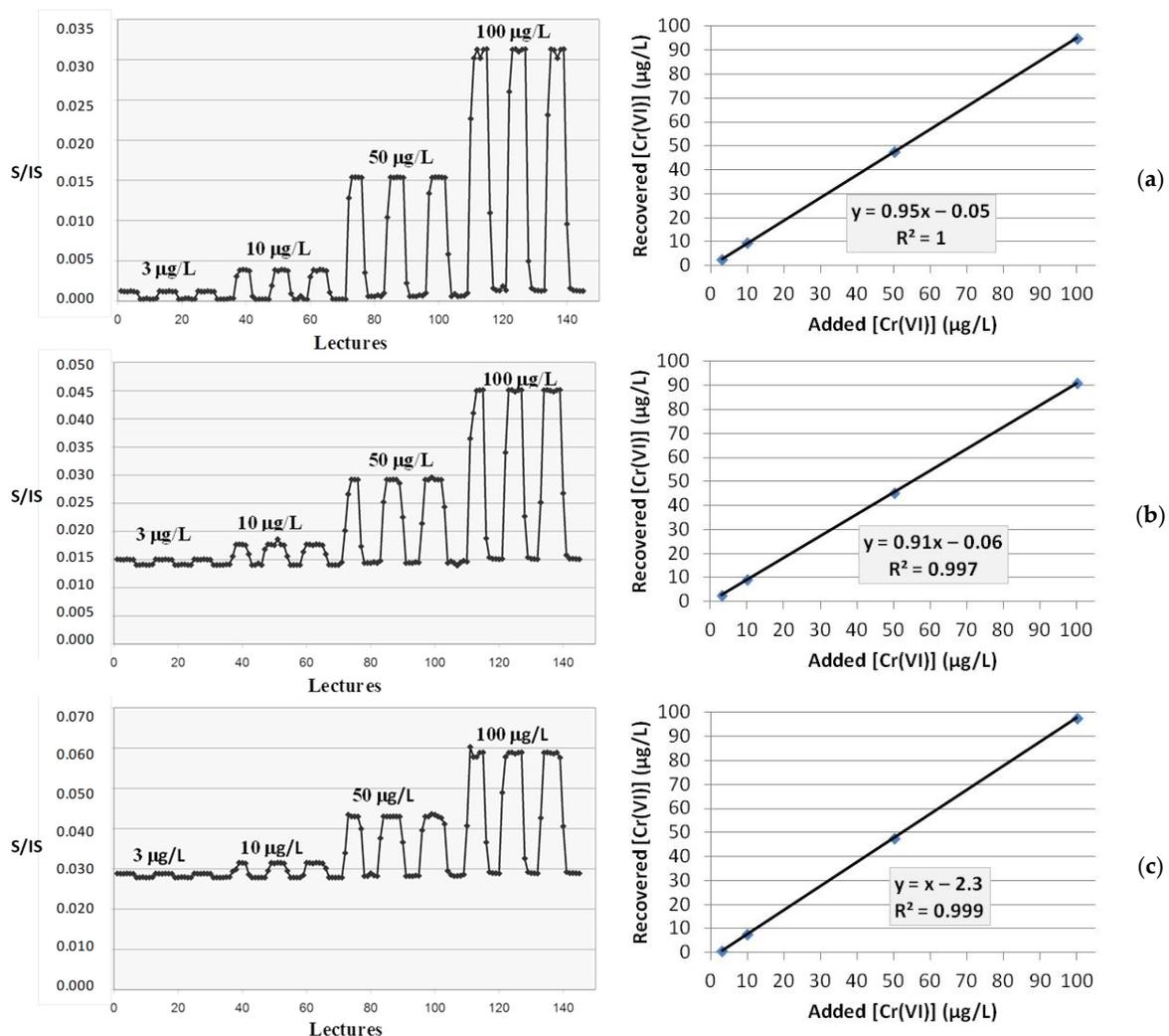
Figure 6. On-line reading of the feed solution containing: (**a**) [Cr(VI)] in the range of 3–100 µg/L in the absence of [Cr(III)]initial; (**b**) [Cr(VI)] in the range of 3–100 µg/L and [Cr(III)] = 50 µg/L; (**c**) [Cr(VI)] in the range of 3–100 µg/L and [Cr(III)] = 100 µg/L.

The baseline is given by the measurement of Cr(III), while the height of the step represents the measurement of Cr(VI). Moreover, it can be noticed that upon increasing the Cr(III) concentration, there is a slight drift in the baseline due to a small amount of Cr(III) that is not removed from the TMC. The error in evaluating the Cr(III) concentration, which is not higher than 5%, is more relevant when the concentration of Cr(VI) is higher. Figure 6 also shows the response curves of the S/IS values based on known Cr(VI) concentrations. The slope of the lines, which can be considered a measure of the E% of Cr(VI), is very good in all cases, with an R^2 that is always higher than 0.99 and a slope in the range of 0.90–1.0. The intercept values are not equal to 0 because only in the ideal conditions (100% Cr(VI) removal efficiency) the lines should have the slope at 1 and intercept at 0. Subsequently, the method was validated using two real samples of tap water and eluate of municipal solid waste, fortified with Cr(VI) in amounts ranging from 10 to 100 μg/L. The results are shown in Figure 7.
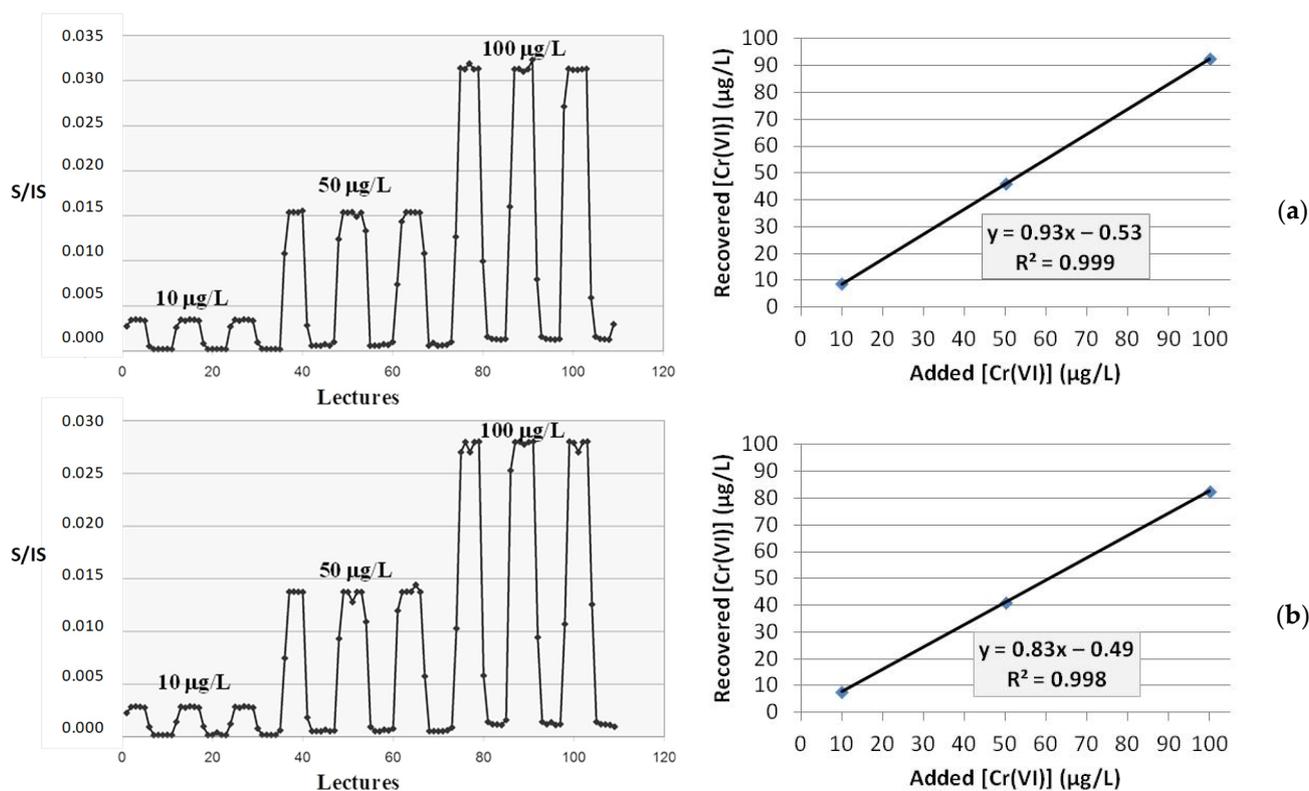
Figure 7. On-line reading of solutions of (**a**) tap water and (**b**) eluate of urban solid waste fortified with increasing amounts of Cr(VI) in the range of 10–100 μg/L.

The E% for tap water is comparable to that obtained using standard solutions in deionized water, with efficiencies higher than 90% within the range of concentrations examined, while in the case of the eluate, it is possible to notice a loss of linearity, clearly evident at low concentrations of Cr(VI), with a lower slope observed for the straight line. This indicates the presence of a matrix effect due to the complexity of the examined sample. This problem can be solved by calibrating with the standard additions method by adding a known concentration of Cr(VI) to the feed solution. In fact, with its application to this sample, the results were satisfactory in terms of extraction efficiency and slope achieved.

3.3. Study Limitation

The present study has some limitations. First of all, the TCM preparation is not an easy task since two peristaltic pumps are needed and a 4-way valve. Because the carrier is an ion-exchanger, it can interact with any anion present in the solution and reduce the

Cr(VI) transport efficiency, affecting the system's accuracy. More information on possible interference is therefore necessary.

4. Conclusions

In this work, a new hollow fiber contactor was designed. The system is able to carry out both the Cr(VI) extraction and stripping steps in a single module, overcoming the disadvantages of double-module systems including low efficiency, large volumes of the membrane solution and the discontinuity of the extraction and stripping operations. Furthermore, the designed contactor is able to work for both separation and preconcentration purposes, and when interfaced with ICP-OES, it provides an on-line measurement of Cr(VI) and Cr(III), even at concentrations at the $\mu g/L$ level. This system is easily automated and can be operated under continuous flow, with a significant advantage for environmental monitoring applications. The coupling of the two instruments showed a good analytical performance even at low concentrations of Cr. In particular, the coefficient of variation percentage (CV%) of the measurements was approximately 5%, and the E% of Cr(VI) was always higher than 90%. The system is subject to the matrix effect, in which case the method's performance could be improved by the standard additions method. It should be noted that the approach used for the separation between Cr(III) and Cr(VI) could be extended to other applications in which one element can be present in a positive or negative state with an appropriate choice of carrier and operating conditions.

5. Patents

Patent application number 1020200004138 was filed with the Italian Patent and Trademark Office (UIBM) on 27 February 2020.

Supplementary Materials: The following are available online at https://www.mdpi.com/2227-9717/9/3/536/s1, S1: Hollow fiber membrane contactor; S2: Optimization of the ICP-OES parameters; Figure S1: (**a**) Scheme of the upper end of the annular contactor; (**b**) Detail of the fiber fixing system; Figure S2: Percentage recoveries (R%) using standard solutions; Figure S3: Signal of the analyte (S) relative to the internal standard signal (IS) according to the number of readings with replicate read time of 20 s; [Cr(VI)]initial = 60 $\mu g/L$, [Cr(III)]initial = 30 $\mu g/L$.

References

1. Avudainayagam, S.; Megharaj, M.; Owens, G.; Kookana, R.S.; Chittleborough, D.; Naidu, R. Chemistry of chromium in soils with emphasis on tannery waste sites. *Rev. Environ. Contam. Toxicol.* **2003**, *178*, 53–91. [PubMed]
2. Lunk, H.J. Discovery, properties and applications of chromium and its compounds. *ChemTexts* **2015**, *1*, 1–17. [CrossRef]
3. Canepari, S.; Castellano, P.; Astolfi, M.L.; Materazzi, S.; Ferrante, R.; Fiorini, D.; Curini, R. Release of particles, organic compounds, and metals from crumb rubber used in synthetic turf under chemical and physical stress. *Environ. Sci. Pollut. Res.* **2015**, *25*, 1448–1459. [CrossRef]

4. Tajima, H.; Yoshida, T.; Ohnuma, A.; Fukuyama, T.; Hayashi, K.; Yamaguchi, S.; Ohtsuka, R.; Sasaki, J.; Tomita, M.; Kojima, S.; et al. Pulmonary injury and antioxidant response in mice exposed to arsenate and hexavalent chromium and their combination. *Toxicology* **2010**, *267*, 118–124. [CrossRef] [PubMed]

5. Astolfi, M.L.; Marconi, E.; Lorini, L.; Valentino, F.; Silva, F.; Ferreira, B.S.; Canepari, S.; Majone, M. Elemental concentration and migratability in bioplastics derived from organic waste. *Chemosphere* **2020**, *25*, 127472. [CrossRef] [PubMed]

6. Greenwood, N.N.; Earnshaw, A. *Chemistry of the Element*, 2nd ed.; Butterworth-Heinemann: Oxford, UK, 1997.

7. Lai, A.; Astolfi, M.L.; Bertelli, V.; Gatto Agostinelli, V.; Zeppilli, M.; Majone, M. Chromate fate and effect in bioelectrochemical systems for remediation of chlorinated solvents. *New Biotechnol.* **2021**, *60*, 27–35. [CrossRef] [PubMed]

8. World Health Organization (WHO). Trace-elements in human nutrition. Report of a WHO Expert Committee. *Tech. Rep. Ser.* **1973**, *532*, 1–65.

9. Levina, A.; Lay, P.A. Chemical properties and toxicity of chromium(III) nutritional supplements. *Chem. Res. Toxicol.* **2008**, *21*, 563–571. [CrossRef]

10. Bhattacharya, P.T.; Misra, S.R.; Hussain, M. Nutritional aspects of essential trace elements in oral health and disease: An extensive review. *Scientifica* **2016**, *2016*, 1–12. [CrossRef]

11. World Health Organization (WHO)—International Agency for Research on Cancer (IARC). IARC monographs on the evaluation of carcinogenic risks to humans. Chromium, nickel and welding. *Sci. Publ. Ser.* **1990**, *49*, 1–677.

12. Legislative decree n. 30 of 16 March 2009. Available online: https://www.minambiente.it/sites/default/files/D.Lgs_._16-3-2009_n._30.pdf (accessed on 17 March 2021).

13. Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the Protection of Groundwater against Pollution and Deterioration. Available online: https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:372:0019:0031:EN:PDF (accessed on 17 March 2021).

14. Decree 14 November 2016, concerning amendments of the Annex I to Legislative Decree n. 31 of 2 February 2001, on "Implementation of Directive 98/83/ EC on the Quality of Water Intended for Human Consumption". Council Directive 98/83/EC, Off. J. Eur. Comm. L330/32 (1998). Available online: http://extwprlegs1.fao.org/docs/pdf/ita162901.pdf (accessed on 17 March 2021).

15. Rama Jyothi, N.; Mohammad Farook, N.A.; Cho, M.; Shim, J. Analysis and speciation of chromium in environmental matrices by various analytical techniques. *Asian J. Chem.* **2013**, *25*, 4125–4136. [CrossRef]

16. El-Sheikh, A.H.; Abu Hilal, M.M.; Sweileh, J.A. Bio-separation, speciation and determination of chromium in water using partially pyrolyzed olive pomace sorbent. *Bioresour. Technol.* **2011**, *102*, 5749–5756. [CrossRef] [PubMed]

17. Saçmacı, S.; Kartal, S.; Yilmaz, Y.; Saçmacı, M.; Soykan, C. A new chelating resin: Synthesis, characterization and application for speciation of chromium (III)/(VI) species. *Chem. Eng. J.* **2012**, *181–182*, 746–753. [CrossRef]

18. Abdolmohammad-Zadeh, H.; Sadeghi, G.H. A nano-structured material for reliable speciation of chromium and manganese in drinking waters, surface waters and industrial wastewater effluents. *Talanta* **2012**, *94*, 201–208. [CrossRef] [PubMed]

19. Habila, M.; Unsal, Y.E.; Alothman, Z.A.; Shabaka, A.; Tuzen, M.; Soylak, M. Speciation of chromium in natural waters, tea, and soil with membrane filtration flame atomic absorption spectrometry. *Anal. Lett.* **2015**, *48*, 2258–2271. [CrossRef]

20. Liang, P.; Sang, H. Speciation of chromium in water samples with cloud point extraction separation and preconcentration and determination by graphite furnace atomic absorption spectrometry. *J. Hazard. Mater.* **2008**, *154*, 1115–1119. [CrossRef] [PubMed]

21. Mandiwana, K.L.; Panichev, N.; Panicheva, S. Determination of chromium(VI) in black, green and herbal teas. *Food Chem.* **2011**, *129*, 1839–1843. [CrossRef]

22. Moghadam, M.R.; Dadfarnia, S.; Shabani, A.M.H. Speciation and determination of ultra-trace amounts of chromium by solidified floating organic drop microextraction (SFODME) and graphite furnace atomic absorption spectrometry. *J. Hazard. Mater.* **2011**, *186*, 169–174. [CrossRef]

23. Bermejo-Barrera, P.; Barciela-Alonso, M.C.; Pérez-Fernández, B.; Bermejo-Barrera, A. Direct speciation analysis of Cr(VI) by electrothermal atomic absorption spectrometry, based on the volatilization of Cr(III)–thenoyltrifluoracetonate from the graphite furnace. *Spectrochim. Acta B* **2003**, *58*, 167–173. [CrossRef]

24. Zou, A.M.; Tang, X.Y.; Chen, M.L.; Wang, J.H. Preconcentration and speciation of chromium in a sequential injection system incorporating dual mini-columns coupled with electrothermal atomic absorption spectrometry. *Spectrochim. Acta B* **2008**, *63*, 607–611. [CrossRef]

25. Jorge, E.O.; Rocha, M.M.; Fonseca, I.T.E.; Neto, M.M.M. Studies on the stripping voltammetric determination and speciation of chromium at a rotating-disc bismuth film electrode. *Talanta* **2010**, *81*, 556–564. [CrossRef] [PubMed]

26. Swietlik, R.; Molik, A.; Molenda, M.; Trojanowska, M.; Siwiec, J. Chromium (III/VI) speciation in urban aerosol. *Atmos. Environ.* **2011**, *45*, 1364–1368. [CrossRef]

27. Sumida, T.; Sabarudin, A.; Oshima, M.; Motomizu, S. Speciation of chromium in seawater by ICP-AES with dual mini-columns containing chelating resin. *Anal. Sci.* **2006**, *22*, 161–164. [CrossRef]

28. Li, Y.; Hu, B.; Jiang, Z.; Wu, Y. Speciation of chromium in water samples by cloud point extraction combined with low temperature electrothermal vaporization ICP-OES. *Anal. Lett.* **2006**, *39*, 809–822. [CrossRef]

29. Ganjali, M.R.; Babaei, L.H.; Badiei, A.; Saberian, K. A novel method for fast enrichment and monitoring of hexavalent and trivalent chromium at the ppt level with modified silica MCM-41 and its determination by inductively coupled plasma optical emission spectrometry. *Quim. Nova* **2006**, *29*, 440–443. [CrossRef]

30. Narukawa, T.; Riley, K.W.; French, D.H.; Chiba, K. Speciation of chromium in Australian fly ash. *Talanta* **2007**, *73*, 178–184. [CrossRef]
31. Zhang, N.; Suleiman, J.S.; He, M.; Hu, B. Chromium(III)-imprinted silica gel for speciation analysis of chromium in environmental water samples with ICP-MS detection. *Talanta* **2008**, *75*, 536–543. [CrossRef]
32. Markiewicz, B.; Komorowicz, I.; Sajnóg, A.; Belter, M.; Barałkiewicz, D. Chromium and its speciation in water samples by HPLC/ICP-MS—Technique establishing metrological traceability: A review since 2000. *Talanta* **2015**, *132*, 814–828. [CrossRef]
33. Astolfi, M.L.; Di Filippo, P.; Gentili, A.; Canepari, S. Semiautomatic sequential extraction of polycyclic aromatic hydrocarbons and elemental bio-accessible fraction by accelerated solvent extraction on a single particulate matter sample. *Talanta* **2017**, *174*, 838–844. [CrossRef]
34. Monasterio, R.P.; Altamirano, J.C.; Martínez, L.D.; Wuilloud, R.G. A novel fiber-packed column for on-line preconcentration and speciation analysis of chromium in drinking water with flame atomic absorption spectrometry. *Talanta* **2009**, *77*, 1290–1294. [CrossRef]
35. Şahan, S.; Saçmaci, S.; Kartal, S.; Saçmaci, M.; Şahin, U.; Ülgen, A. Development of a new on-line system for the sequential speciation and determination of chromium species in various samples using a combination of chelating and ion exchange resins. *Talanta* **2014**, *120*, 391–397. [CrossRef]
36. Gil, R.A.; Cerutti, S.; Gásquez, J.A.; Olsina, R.A.; Martinez, L.D. Preconcentration and speciation of chromium in drinking water samples by coupling of on-line sorption on activated carbon to ETAAS determination. *Talanta* **2006**, *68*, 1065–1070. [CrossRef] [PubMed]
37. Jia, X.; Gong, D.; Xu, B.; Chi, Q.; Zhang, X. Development of a novel, fast, sensitive method for chromium speciation in wastewater based on an organic polymer as solid phase extraction material combined with HPLC–ICP-MS. *Talanta* **2016**, *147*, 155–161. [CrossRef] [PubMed]
38. Alguacil, F.J.; Alonso, M.; Sastre, A.M. Facilitated supported liquid membrane transport of gold(I) and gold(III) using Cyanex 921. *J. Membr. Sci.* **2005**, *252*, 237–244. [CrossRef]
39. López-López, J.A.; Mendiguchía, C.; Pinto, J.J.; Moreno, C. Liquid membranes for quantification and speciation of trace metals in natural waters. *Trends Anal. Chem.* **2010**, *29*, 645–653. [CrossRef]
40. Zeng, C.; Yang, F.; Zhou, N. Hollow fiber supported liquid membrane extraction coupled with thermospray flame furnace atomic absorption spectrometry for the speciation of Sb(III) and Sb(V) in environmental and biological samples. *Microchem. J.* **2011**, *98*, 307–311. [CrossRef]
41. Güell, R.; Fontàs, C.; Anticó, E.; Salvadó, V.; Crespo, J.G.; Velizarov, S. Transport and separation of arsenate and arsenite from aqueous media by supported liquid and anion-exchange membranes. *Sep. Purif. Technol.* **2011**, *80*, 428–434. [CrossRef]
42. San Román, M.F.; Bringas, E.; Ibañez, R.; Ortiz, I. Liquid membrane technology: Fundamentals and review of its applications. *J. Chem. Technol. Biotechnol.* **2010**, *85*, 2–10. [CrossRef]
43. Guha, A.K.; Majumdar, S.; Sirkar, K.K. Gas separation modes in a hollow fiber contained liquid membrane permeate. *Ind. Eng. Chem. Res.* **1992**, *31*, 593–604. [CrossRef]
44. Sastre, A.M.; Kumar, A.; Shukla, J.P.; Singh, R.K. Improved techniques in liquid membrane separations: An overview. *Sep. Purif. Methods* **1998**, *27*, 213–298. [CrossRef]
45. Dai, X.P.; Yang, Z.F.; Luo, R.G.; Sirkar, K.K. Lipase-facilitated separation of organic acids in a hollow fiber contained liquid membrane module. *J. Membr. Sci.* **2000**, *171*, 183–196. [CrossRef]
46. Mat, N.C.; Lou, Y.; Lipscomb, G.G. Hollow fiber membrane modules. *Curr. Opin. Chem. Eng.* **2014**, *4*, 18–24. [CrossRef]
47. Kavousi, F.; Syron, E.; Semmens, M.; Casey, E. Hydrodynamic and gas transfer performance of confined hollow fibre membrane modules with the aid of computational fluid dynamics. *J. Membr. Sci.* **2016**, *513*, 117–128. [CrossRef]
48. Trivunac, K.; Stevanovic, S.; Mitrovic, M. Pertraction of phenol in hollow-fiber membrane contactors. *Desalination* **2004**, *162*, 93–101. [CrossRef]
49. Kocherginsky, N.M.; Yang, Q.; Seelam, L. Recent advances in supported liquid membrane technology. *Sep. Purif. Technol.* **2007**, *53*, 171–177. [CrossRef]
50. Pabby, A.K.; Sastre, A.M. State-of-the-art review on hollow fibre contactor technology and membrane-based extraction processes. *J. Membr. Sci.* **2013**, *430*, 263–303. [CrossRef]
51. Galán, B.; Calzada, M.; Ortiz, I. Recycling of Cr(VI) by membrane solvent extraction: Long term performance with mathematical model. *Chem. Eng. J.* **2006**, *124*, 71–79. [CrossRef]
52. Güell, R.; Anticó, E.; Salvadó, V.; Fontàs, C. Efficient hollow fiber supported liquid membrane system for the removal and preconcentration of Cr(VI) at trace levels. *Sep. Purif. Technol.* **2008**, *62*, 389–393. [CrossRef]
53. Bey, S.; Criscuoli, A.; Simone, S.; Figoli, A.; Benamor, M.; Drioli, E. Hydrophilic PEEK-WC hollow fibre membrane contactors for chromium(VI) removal. *Desalination* **2011**, *283*, 16–24. [CrossRef]
54. Coker, V.S.; Garrity, A.; Wennekes, W.B.; Roesink, H.D.; Cutting, R.S.; Lloyd, J.R. Cr(VI) and azo dye removal using a hollow-fibre membrane system functionalized with a biogenic Pd-magnetite catalyst. *Environ. Technol.* **2014**, *35*, 1046–1054. [CrossRef]
55. APHA. *Standard Methods for the Examination of Water and Wastewater*; American Public Health Association: Washington, DC, USA, 1995.
56. Saf, A.O.; Alpaydin, S.; Coskun, A.; Ersoz, M. Selective transport and removal of Cr(VI) through polymer inclusion membrane containing 5-(4-phenoxyphenil)-6H-1,3,4-thiadiazin-2-amine as carrier. *J. Membr. Sci.* **2011**, *377*, 241–248. [CrossRef]

57. Alpaydin, S.; Saf, A.Ö.; Bozkurt, S.; Sirit, A. Kinetic study on removal of toxic metal Cr(VI) through a bulk liquid membrane containing p-tert-butylcalix[4]arene derivative. *Desalination* **2011**, *275*, 166–171. [CrossRef]

58. Parinejad, M.; Yaftian, M.R. A study on the removal of chromium(VI) oxoanions from acid solutions by using oxonium ion-crown ether complexes as mobile carrier agents. *Iran. J. Chem. Chem. Eng.* **2007**, *26*, 19–27.

59. Usapein, P.; Lothongkum, A.W.; Ramakul, P.; Pancharoen, U. Efficient transport and selective extraction of Cr(VI) from waste pickling solution of the stainless steel-cold rolled plate process using Aliquat 336 via HFSLM. *Korean J. Chem. Eng.* **2009**, *26*, 791–798. [CrossRef]

60. Bucci, R.; Canepari, S.; Cardarelli, E.; Girelli, A.M.; Pietrodangelo, A.; Valiente, M. Carrier-mediated transport of amino acids through bulk liquid membranes. *Sep. Sci. Technol.* **2004**, *39*, 3821–3838. [CrossRef]

61. Chaudry, M.A.; Bukhari, N.; Mazhar, M.; Tazeen, F. Vanadium(V) ions transport through tri-n-octyl amine cyclohexane supported liquid membranes. *Sep. Purif. Technol.* **2007**, *54*, 227–233. [CrossRef]

62. Zaghbani, A.; Tayeb, R.; Dhahbi, M. Studies on the transport of chromium(III) through a supported liquid membrane containing D2EHPA as carrier. *Desalin. Water Treat.* **2009**, *12*, 247–255. [CrossRef]

63. Djane, N.K.; Ndung'u, K.; Jhonsson, C.; Sartz, H.; Tornstrom, T.; Mathiasson, L. Chromium speciation in natural waters using serially connected supported liquid membranes. *Talanta* **1999**, *48*, 1121–1132. [CrossRef]

64. Dermatas, D.; Mpouras, T.; Chrysochoou, M.; Panagiotakis, I.; Vatseris, C.; Linardos, N.; Theologou, E.; Boboti, N.; Xenidis, A.; Papassiopi, N.; et al. Origin and concentration profile of chromium in a Greek aquifer. *J. Hazard. Mater.* **2015**, *281*, 35–46. [CrossRef]

65. Diniz, K.M.; Tarley, C.R.T. Speciation analysis of chromium in water samples through sequential combination of dispersive magnetic solid phase extraction using mesoporous amino-functionalized Fe_3O_4/SiO_2 nanoparticles and cloud point extraction. *Microchem. J.* **2015**, *123*, 185–195. [CrossRef]

66. Catalani, S.; Fostinelli, J.; Gilberti, M.E.; Apostoli, P. Application of a metal free high performance liquid chromatography with inductively coupled plasma mass spectrometry (HPLC–ICP-MS) for the determination of chromium species in drinking and tap water. *Int. J. Mass Spectrom.* **2015**, *387*, 31–37. [CrossRef]

67. Bahadir, Z.; Bulut, V.N.; Hidalgo, M.; Soylak, M.; Margui, E. Cr speciation in water samples by dispersive liquid–liquid microextraction combined with total reflection X-ray fluorescence spectrometry. *Spectrochim. Acta B* **2016**, *115*, 46–51. [CrossRef]

68. Hu, L.; Cai, Y.; Jiang, G. Occurrence and speciation of polymeric chromium(III), monomeric chromium(III) and chromium(VI) in environmental samples. *Chemosphere* **2016**, *156*, 4–20. [CrossRef] [PubMed]