Development of an online ultrasensitive method for preconcentration and speciation of Cr(III)/Cr(VI) in aqueous samples

Emerging pollutants in aquatic ecosystems

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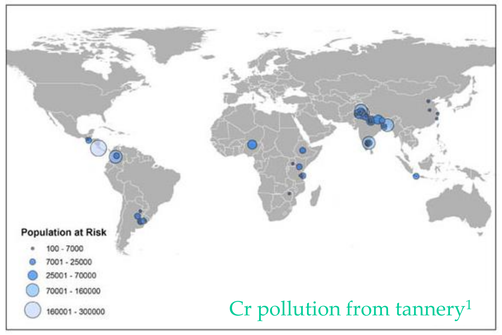
Background

Chromium appears at the hydrosphere due to the tannery industry. In these aquatic systems, Cr^{III} and Cr^{VI} are the species found, both of them with opposites effects in human health. Cr ^{VI} is a powerful carcinogen, so development of new methods for the preconcentration, speciation and quantification of these species is essential for water health.



Cr pollution from tannery[1]

Main risks of Cr^{VI}

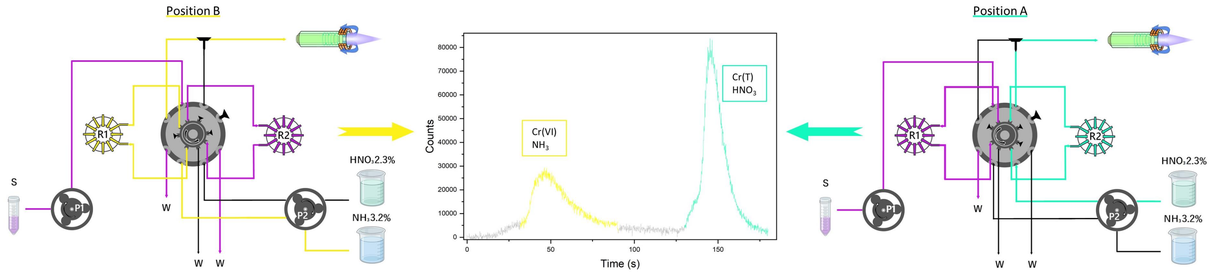
- Liver Damage
- Lung Cancer
- Reproductive Problems
- Developmental Harm

Development of the "Cr^{VI} toxicity"

- **1987** – Chinese scientist Zhan JianDong publishes study showing a strong link between drinking water with chromium-6 and stomach cancer.
- **1991** – EPA sets national drinking water regulation for total chromium, with no separate rule for chromium-6.
- **1992** – Erin Brockovich investigates chromium-6 pollution in the tap water of Hinkley, Calif.
- **1996** – Pacific Gas and Electric Company pays $333 million to settle claims of Hinkley residents.
- **1997** – Revision of Zhan's 1987 paper is published, reversing earlier finding.
- **2000** – Film "Erin Brockovich" released.
- **2001** – California lawmakers order legal limit for chromium-6 in drinking water, to take effect by 2004. A California state scientist discovers Zhan's revised paper was written by PG&E consulting firm.
- **2011** – EPA adds chromium-6 to unregulated contaminants for which local utilities must test.

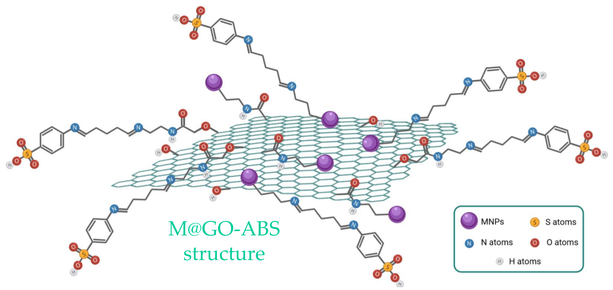
Methodology

In this work, a new online MSPE-ICP-OES method has been developed, employing a novel material: M@GO-ABS, is magnetically confined inside a reactor (R), a pair of these are coupled to a FIAS valve, designed for the sequential load and elution of both reactors. The selective elution is carried by NH_3 as the selective eluent for Cr^{VI} meanwhile total Cr is eluted with HNO_3. Cr^{III} is obtained by difference.

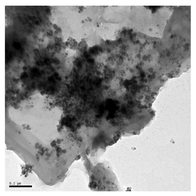


ICP-OES results for the Cr^{VI} (yellow) and Cr^{T} (blue) employing the new developed method

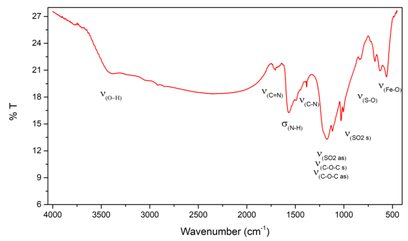
New nanomaterial (patented by the investigation team), M@GO-ABS is based in the coupling of GO and MNPs, allowing a magnetic and simple solid phase extraction. Moreover, sulfanilic acid is introduced in order to provide better selectivity for Cr. The material is characterized by TEM, SEM, IR, MS, XPS, CHN and adsorption isotherm.



M@GO-ABS structure



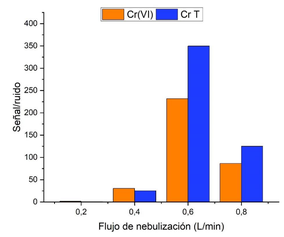
TEM 0'2 μm



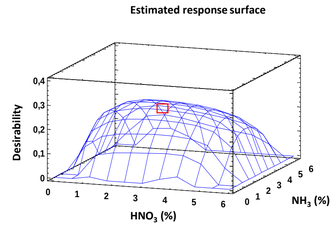
FT-IR of M@GO-ABS

Optimization and validation

Experimental (eluents and their concentration, pH) and instrumental (flows, step times and plasma conditions) parameters were optimized by CCD.



Nebulation flow study



Eluent concentration study

Conclusions

The method was tested with several certified samples, such as fortified lake water, moreover, figures of merit obtained are better than the previously described in bibliography.

In order to apply the methodology, several samples from sea, river, tap and well water were studied. It was proven the utility of the method and recognised the difference of Cr between surface and groundwater, being Cr^{VI}, the toxic specie the most abundant one in surface waters, due to the oxidant atmosphere, being the method able to measure ultratrace levels.

This way, a new, fast, automatic, sensitive, simple and economic method has been obtained for the Cr speciation, based on the eluents selectivity and the novel nanomaterial M@GO-ABS[2]. Furthermore the extraction yield of the nanomaterial, becomes it promising for water remediation and it is currently a via on study.

Analytical applications

Sample	Cr certificate (μgL^{-1})	Added (μgL^{-1})		Recovery (%)		
		$Cr^{III}_{Add.}$	$Cr^{VI}_{Add.}$	$Cr^{III}_{Add.}$	$Cr^{VI}_{Add.}$	Cr^{T}
SPS-SW2	10±0.05	-	-	-	-	-
		50	50	107	106	109
		100	100	95	92	95
TMDA	282±18	-	-	-	-	-
		50	50	112	108	110
		100	100	111	99	105
Sea water GM	-	-	-	-	-	-
		100	100	108	98	103
		200	200	97	98	97
Sea water TX	-	-	-	-	-	-
		200	200	91	91	91
		300	300	98	94	96

Bibliography

1. Blacksmith Institute via https://www.worstpolluted.org/
2. Montoro-Leal, P., García-Mesa, J. C., López Guerrero, M. D. M., Vereda Alonso, Patente ES 2 844 942 B2 Material compuesto absorbente de metales basado en óxido de grafeno magnético y procedimiento de obtención, concedida con fecha 24 Nov'21

Acknoledgements

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"Sea" more

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