

Carbon dots (CDs) as a fluorescent nano-sensor for chromium (VI) determination in water and soil samples.

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Abstract

A simple and fast spectrofluorimetry method based on CDs was proposed to Cr(VI) determination in water and soil samples.

Introduction

CDs are carbon nanoparticle luminescent materials. CDs possess benefits such as low toxicity, environmental friendliness and ease of synthesis route.¹ Recently, CDs have been employed as analytical nano-sensors to quantify potentially toxic metals.² Among those metals, the Cr(VI) is well-known by its carcinogenic and toxic effects for both humans and animals, even at low concentrations. So, this work aimed to develop an analytical method to quantify Cr(VI) in different water and soil samples exploring the interaction process with CDs and spectrofluorimetric detection.

Results and discussion

CDs were synthesized from citric acid with incorporation of glutathione (GSH) by pyrolysis at 270°C. Maximum excitation wavelength was determined as 350 nm where the photoluminescent quantum yield (ϕ) was determined as 69%. The quenching mechanism was evaluated according to the temperature effect (23 to 38°C) and variation of Stern-Volmer ($K_{SV} = 1.92-1.69 \times 10^3 \text{ L mol}^{-1}$) and binding constant ($K_b = 4.59-2.22 \times 10^3 \text{ L mol}^{-1}$) indicates the static quenching mechanism. Based on the K_b variance as a function of temperature along with the Van't Hoff equation, the thermodynamic parameters were calculated, being $\Delta H = -37.3 \text{ KJ mol}^{-1}$; $\Delta S = -55.4 \text{ KJ mol}^{-1}$ and $\Delta G = -20.5 \text{ KJ mol}^{-1}$. According to $\Delta G < 0$, the interaction process was spontaneous whereas $\Delta H < 0$ and $\Delta S < 0$ are innate of Van der Waals interactions and hydrogen bonds. The Table 1 shows the results of chemical optimization for the proposed method. A total of 24 possibly interference ions were evaluated. Al(III) and Pb(II) were the most interference species. Nevertheless, to eliminate these interferences, a Dowex 50W-8X cationic resin was utilized. The proposed method show as figures of merit: LOQ = 0.07 mg L^{-1} , linear range from 0.25 to 12 mg L^{-1} and RSD = 2.15 and 4.65% for Cr(VI) at 1 and 10 mg L^{-1} , respectively. According to the maximum allowable Cr(VI) concentration in water samples established by the CONAMA N° 357 resolution (brackish water

1.1 mg L^{-1}), the proposed method can be utilized for Cr(VI) in real water samples. The method validation was carried out by a recovery assay in fresh, brackish, drinking and tap samples water. Results of samples analysis from the recovery assay are shown in Table 2.

Table 1. Optimized chemical parameters.

Parameter	Evaluated conditions	Selected condition
pH	2 – 10	7
Buffer	Tris, PBS, Hepes, Pipes	Tris
Buffer concentration (mM)	5 – 80	60
CDs concentration (mg L^{-1})	0.09 – 0.53	0.13
Ionic strength (mM)	0 – 300	10

Table 2. Recovery assay in the water samples.

Water type	Cr(VI) added (mg L^{-1})	Cr(VI) recovery (mg L^{-1})	% recovery
Brackish	-	0.28	-
	2	2.37	118
	4	4.21	105
	8	8.45	106
Freshwater	-	< LOD	-
	2	2.09	105
	4	3.80	95.0
	8	8.16	102
Mineral	-	< LOD	-
	2	2.02	101
	4	3.75	93.8
	8	7.78	97.3
Drinkable	-	< LOD	-
	2	2.01	101
	4	3.60	90.0
	8	8.01	100

The recovery values obtained in the water samples indicated the accuracy of the proposed method exploring the CDs. Additionally, the method was applied in the soil samples presented quantitative recoveries.

Conclusions

The proposed method shows a lower LOQ than the maximum allowable Cr(VI) concentration established by the CONAMA N° 357 resolution and similar to other works on the literature.^{2,3} Finally, the method is suitable for Cr(VI) determination in different water and soil samples.

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