TRACE DETECTION OF Cr(VI) -ASSEMBLY OF NanoPARTICLES/CHIT/MULTIWALLED CNTs AS NOVEL ELECTROCHEMICAL SENSOR

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INTRODUCTION

There are significant amounts of Cr into environment through poorly regulated disposal of chromium

Cr enters into the environment via plating, steel, and paint industries [

Chromium exists in two oxidation states (Cr(III) and Cr(VI)).

Cr(VI) - second most inorganic contaminant in groundwater at hazardous waste site

Malik, Bashir, Qureashi, & Pandith, 2019; Covarrubias & Peña Cabriales, 2017; Beltrán & Gómez, 2015

https://www.aguasresiduales.info/revista/blog/contaminacion-del-agua-con-cromo

INTRODUCTION

Cr(VI)

- *High* persistence
- Bioaccumulates
- Severe toxicity
- Carcinogenic

In membrane cell:

Cr(VI) +3e -→ Cr(III)____DNA

Alteration of components in cell

Due to the high toxicity of Cr(VI) and its presence in the environment, effective and reliable monitoring of the species is required.

Malik, Bashir, Qureashi, & Pandith, 2019; Covarrubias & Peña Cabriales, 2017; Beltrán & Gómez, 2015

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INTRODUCTION

0.05 mg·L-1 -------World Health Organization (WHO) as the provisional guideline value for Cr(VI) in groundwater.

.100 mg·L-1 ___Regulated by the Environmental Protection Agency (EPA) for total chromium in drinking water.

http://www.afirm-group.com/wp-content/uploads/2019/09/afirm_chromium_VI_spanish_v2.pdf

Several methodologies including spectral, chromatographic and electrochemical techniques have been developed for the detection of Cr(VI)

The selective detection of Cr(VI) is a challenging task because it suffers from interference due to Cr(III), which exists in relatively high concentration in natural water

Most of the electrochemical techniques are based on the preconcentration of Cr(VI) species on the electrode surface using complexing agent

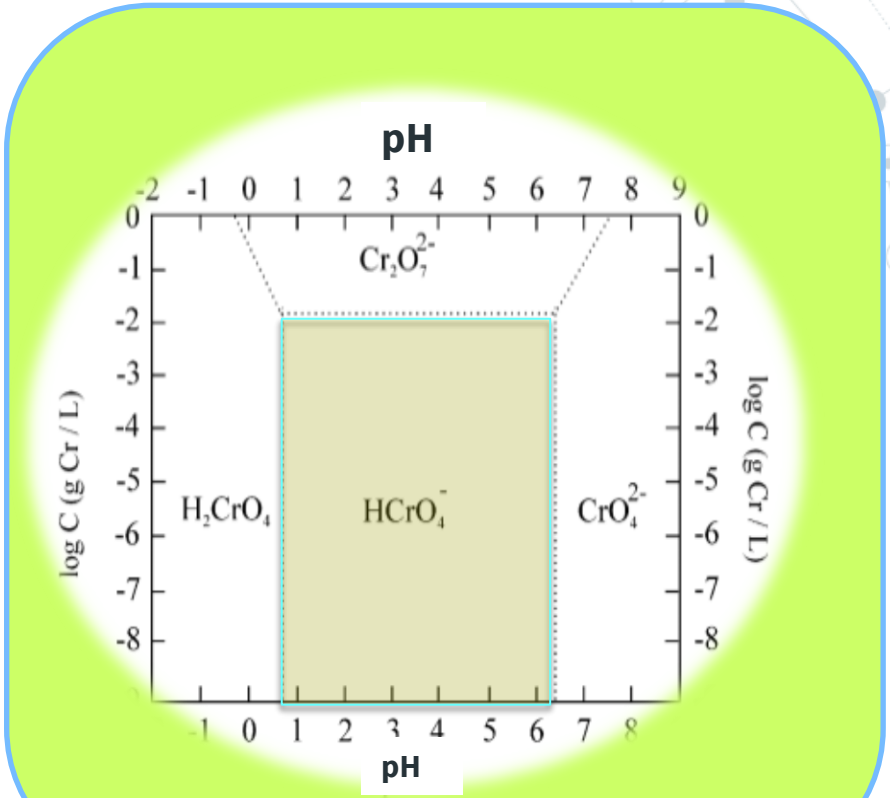
Pourbaix Diagram
Relative domain of Cr (VI) in aqueous media @25 ◦C.

Chemical reactions, low concentration of Cr(VI):

$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+$$
$$HCrO_4^- \leftrightarrow CrO_4^{-2} + H^+$$

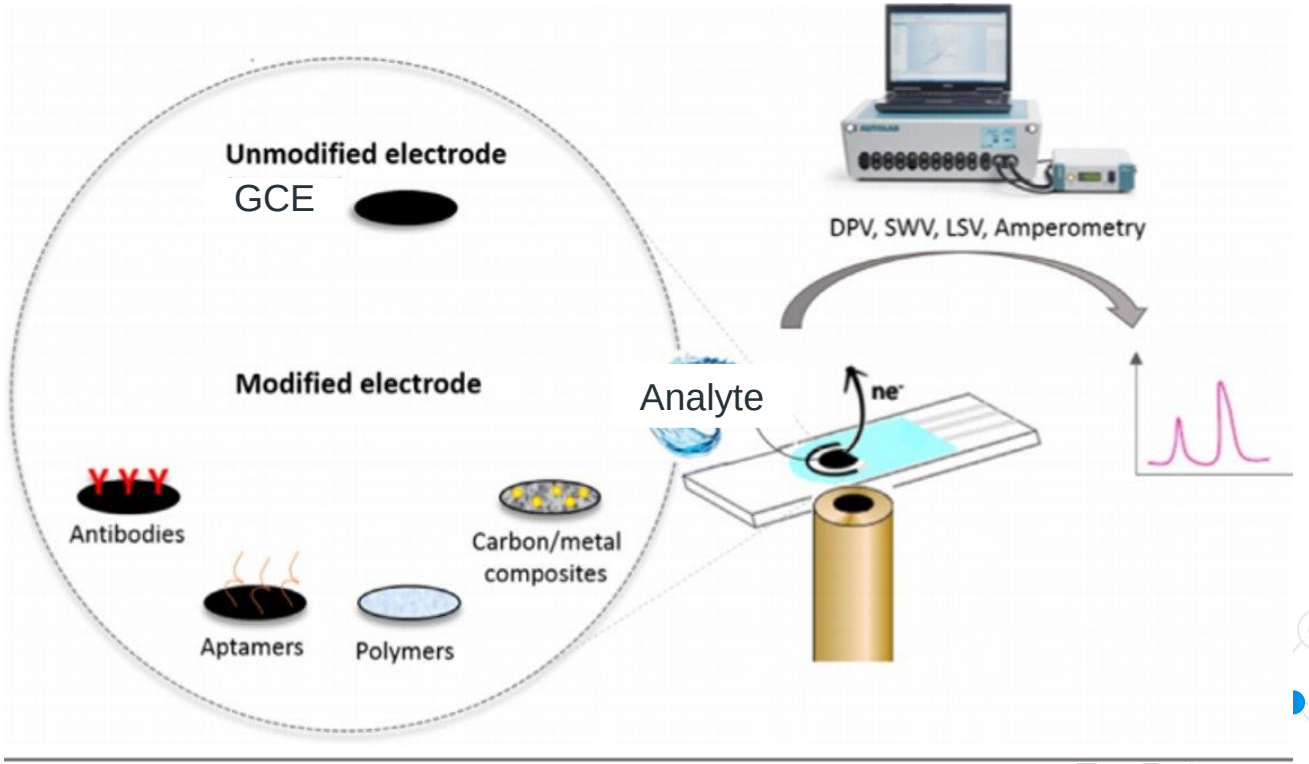
Chemical reaction at concentration of Cr(VI) 1 g·L^{-1}

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{-2} + H_2O$$



Development of highly sensitive analytical methodology for the **detection of trace level** of **toxic chromium species** is of significant interest in analytical chemistry.

Trace Level Electrochemical Detection



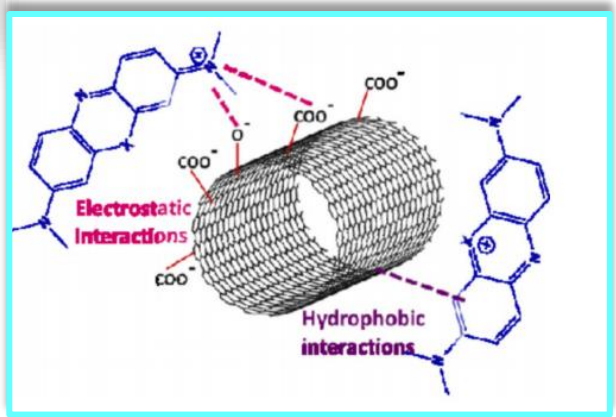
Project: Nanostructured electrode = Sensor

Nanomaterials

1

Multiwalled carbon nanotubes (MWCNT)

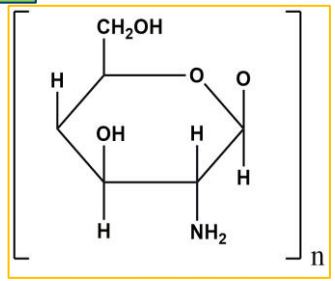
- High electric conductitivy and electronic connection
- Wide electrochemical window for quantification simultaneously of several analytes.
- High surface/volumen ratio for adsoprtion processes and electronic transfer



Project:

Nanomaterials

2



Biopolymer: Chitosan

High adsorption capacity

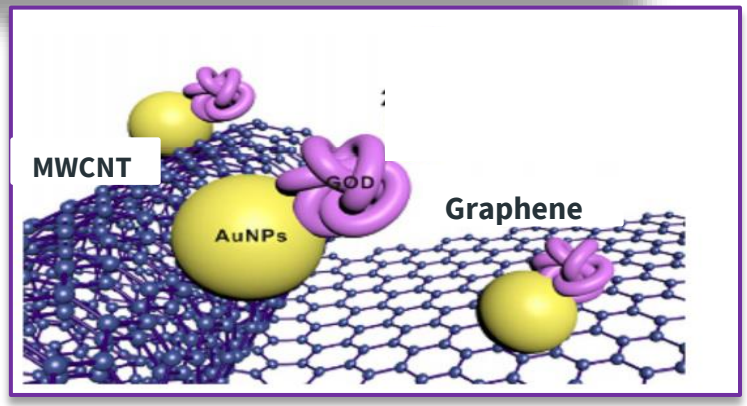
Biofilm formation ability

Important adherence to heavy metal ions.

3

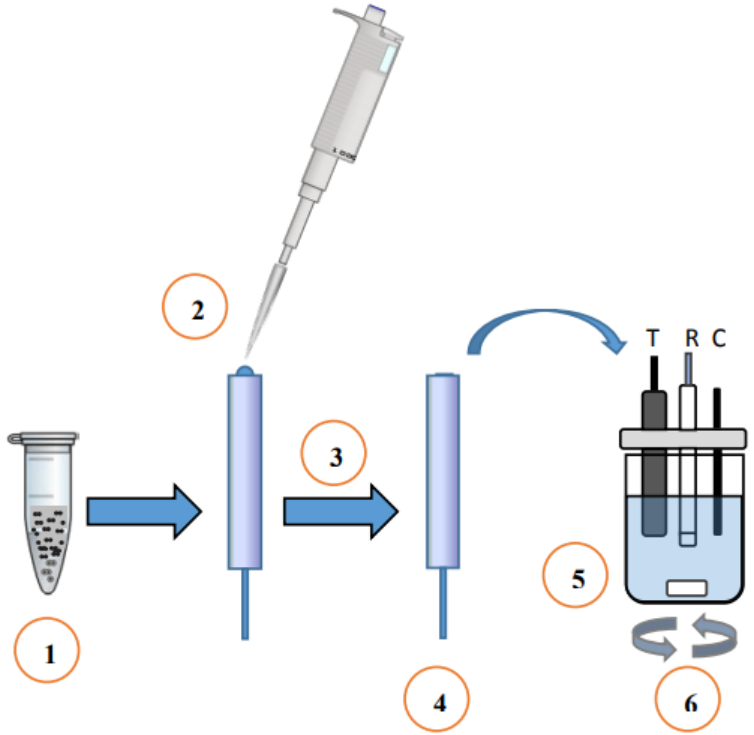
Gold Metallic Nanoparticles(NPs)

- High surface/volumen ratio
- Surface reactivity
- High electric conductivity
- High catalytic capacity



Materials and Methods

1. *GCE chemically modified with multiwalled carbón nanotubes and chitosan (MWCNT/CTS)*



Electrochemical characterization

- -CV
- -EIS

Materials and Methods

2. *MWCNT/CTS/GCE chemically modified electrode coated with electrodeposited gold nanoparticles*

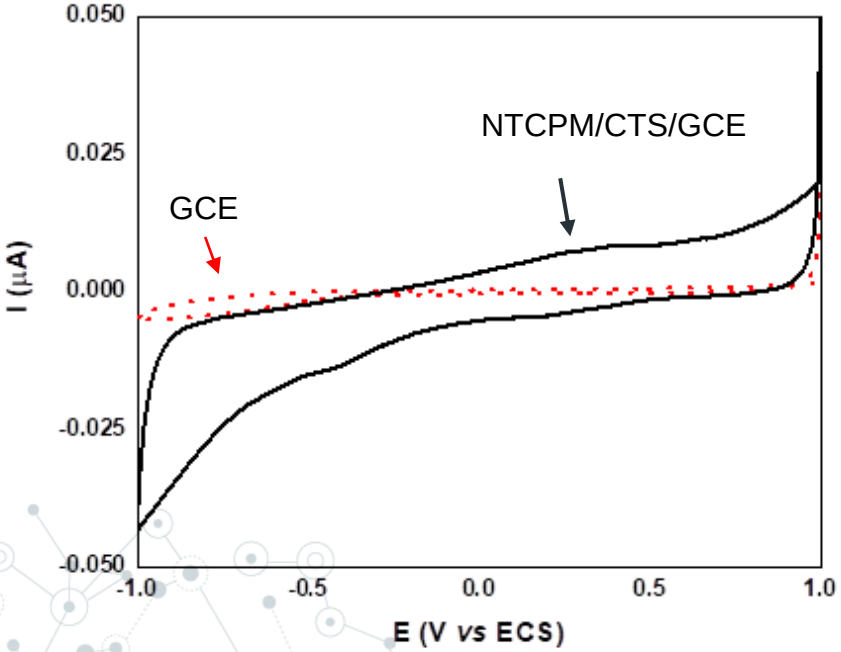
- **Cyclic voltammetry of 1 mM $HAuCl_4$ in 0.5 M de H_2SO_4 on GCE**
- **Cyclic voltammetry of AuNPs/MWCNT/CTS/CGE in 0.5 M de H_2SO_4**

Electrochemical characterization and Morphology Analysis

- **EIS**
- **SEM**

Characterization of modified electrode

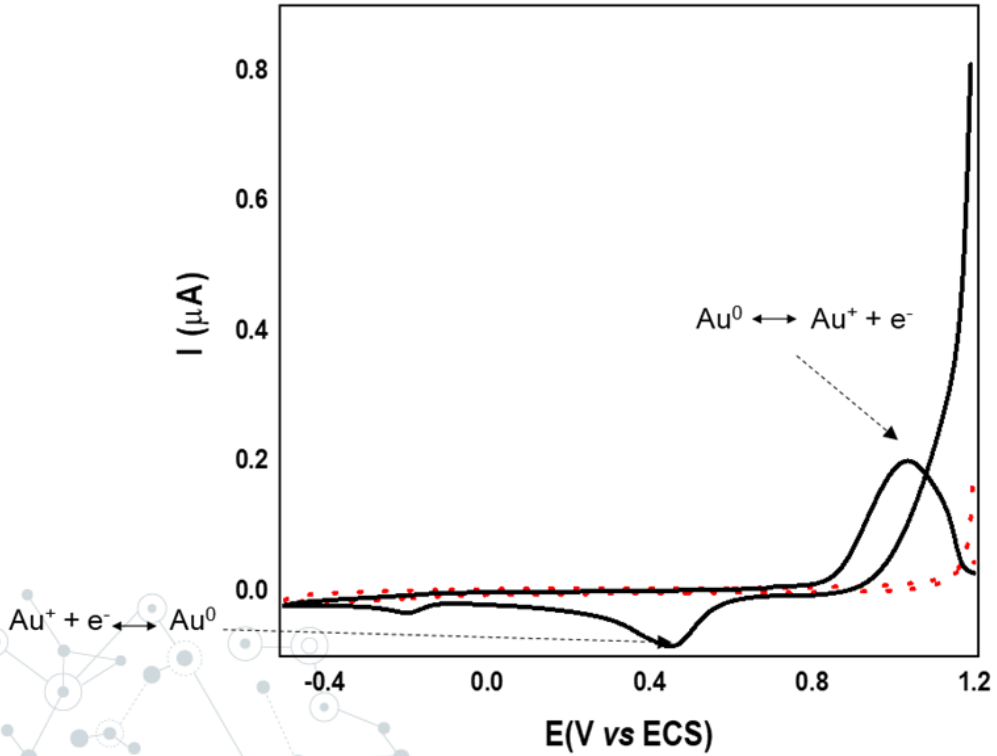
Voltammetric Behaviour of 0.1M HCl, in chemically modified electrode MWCNT/CTS/GCE



- Voltammetry response of Supporting Electrolyte (**red** line) onto glassy carbon electrode
- Voltammetry response of chemically modified electrode MWCNT/CTS/GCE (**black** line)

Preliminary Results

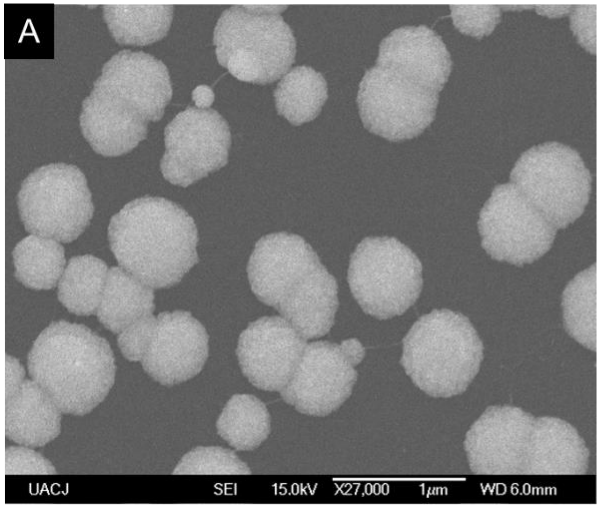
Determination of the electrochemical potential, Ep, for gold electrodeposition

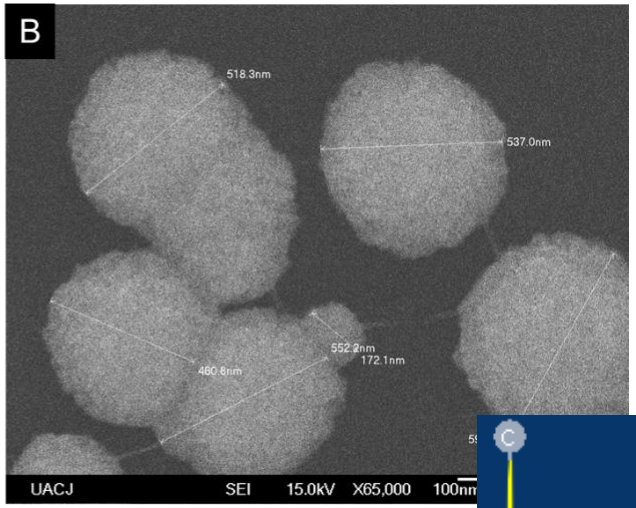


- CV of 1 mM $HAuCl_4$ in 0.5 M H_2SO_4 onto GCE (**black** line)
- CV of 0.5 M H_2SO_4 onto GCE (**red** line).

Preliminary Results

Surface characterization of AuNPs/MWCNT/CTS electrode

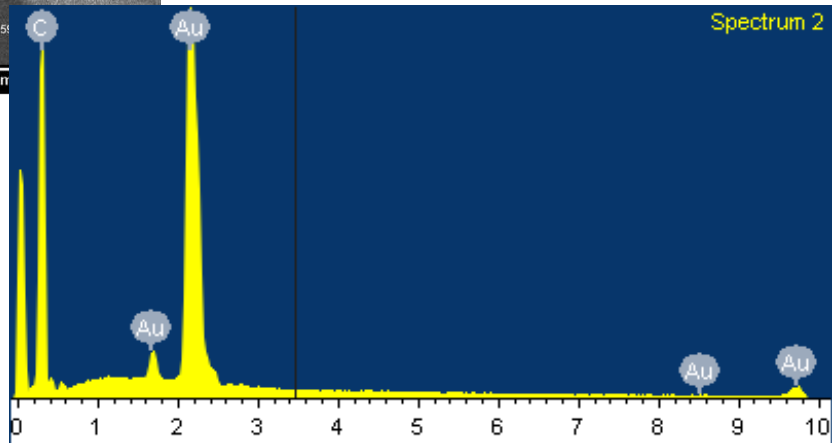




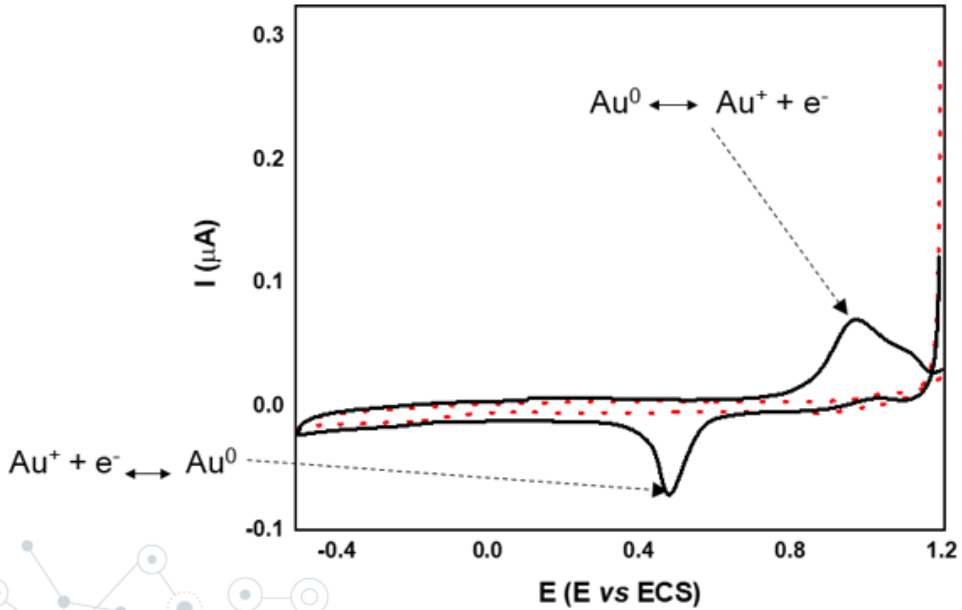
SEM images of MWCNT/CTS/ECV with AuNPs: A)27,000X SEI, B)65,000X y c) 140,000X

EDS Chemical composition

Au-Predominance

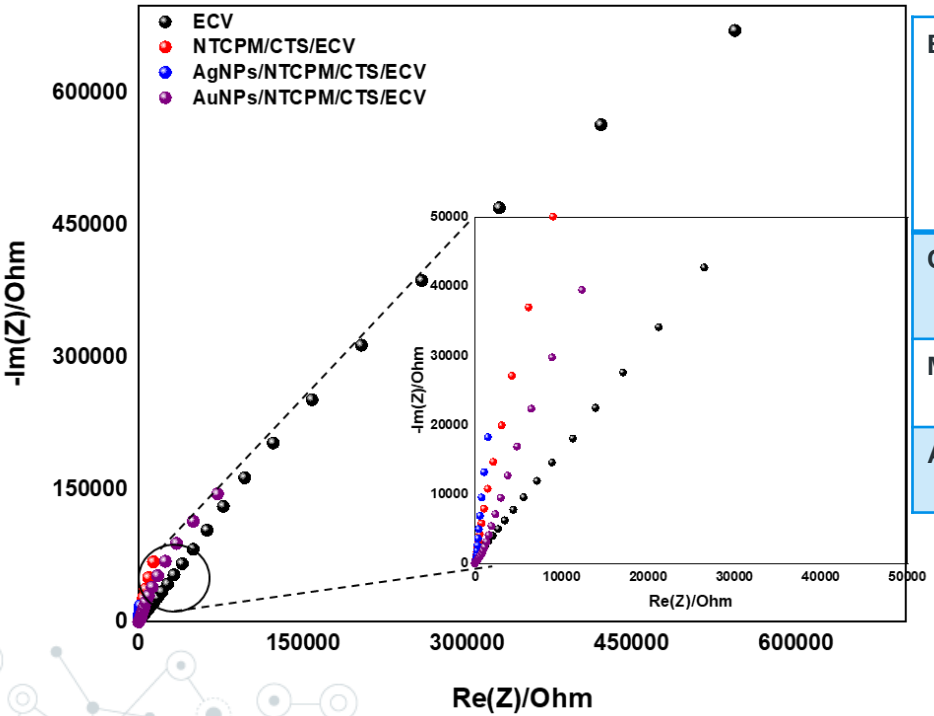


Electrochemical characterization of AuNPs/NTCPM/CTS electrode



- Voltammetry response of Supporting Electrolyte (**red** line) onto GCE
- Voltammetry response of chemically modified electrode AuNPs/NTCPM/CTS (**black** line)

EIS results for the different electrochemical sensors



Electrode	R_s (Ω)	R_{tc} Ωx10^6	Q ($F \cdot s^{n-1} cm^{-2}$)	S ($Ohm \cdot s^{-1/2}$)	a
GCE	147.00	**3.54**	14.80 x 10^{-6}	-535894	0.7
MWCNT/CTS/GCE	71.69	**1.03**	0.18 x 10^{-3}	-16905	0.9
AuNPs/MWCNT/CTS/GCE	78.16	**0.088**	0.27 x 10^{-3}	3596	0.8

Materials and Methods

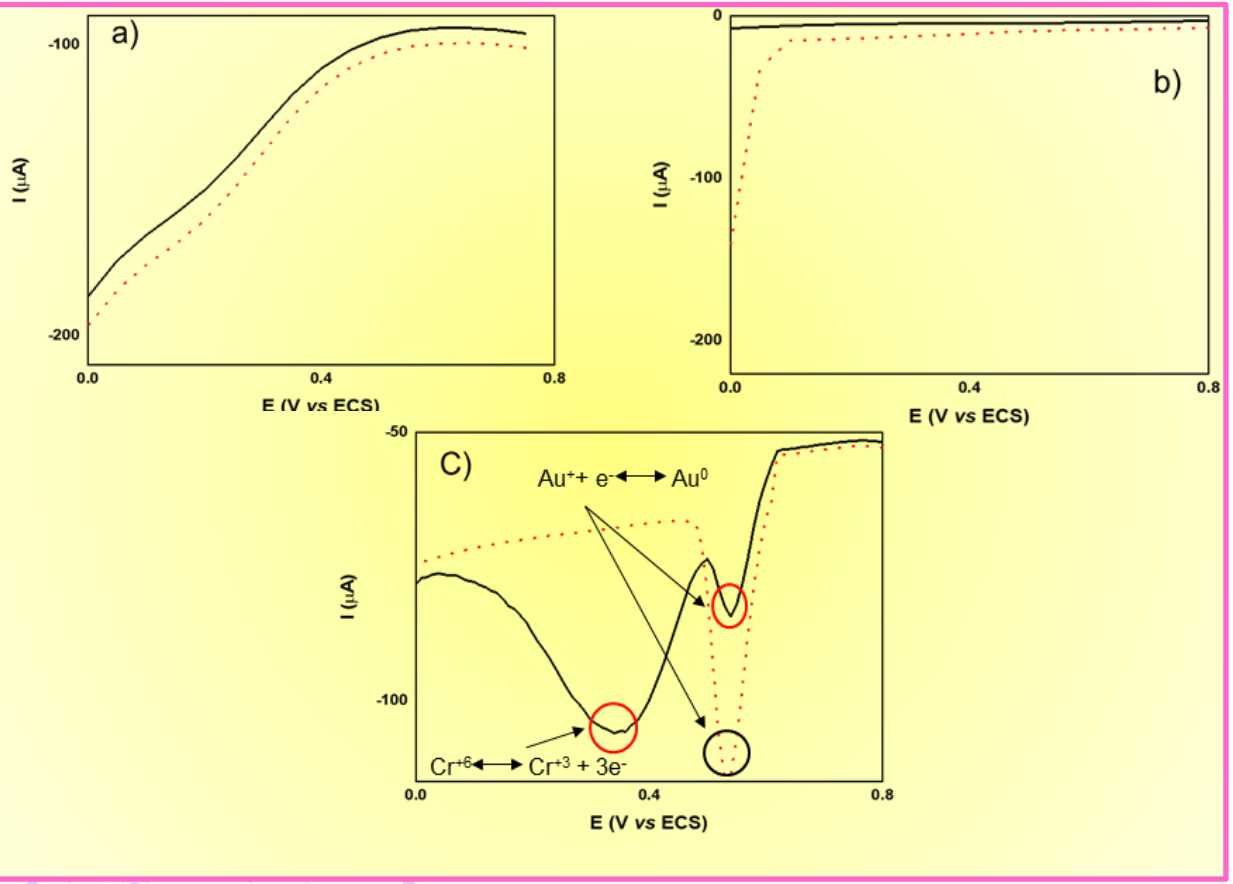
4. *Electrochemical detection of Chromium (VI)*

- **Dissolution of 1 ppb Cr(VI) in HCl 0.1 M**
- **Differential Pulse Voltammetry (DPV)**

Calibration Plot Preparation

- **Linear regression. Interval of Cr(VI) 0.003 to 0.100 ppb**
- **Detection and Quantification Limit (LOD, LOQ)**
- **Accuracy**
- **Precision**

Options for Cr(VI) Electrochemical Detection



Electrochemical determination of 1ppb(1 $\mu g \cdot L^{-1}$) of Cr(VI)

in solid black line.

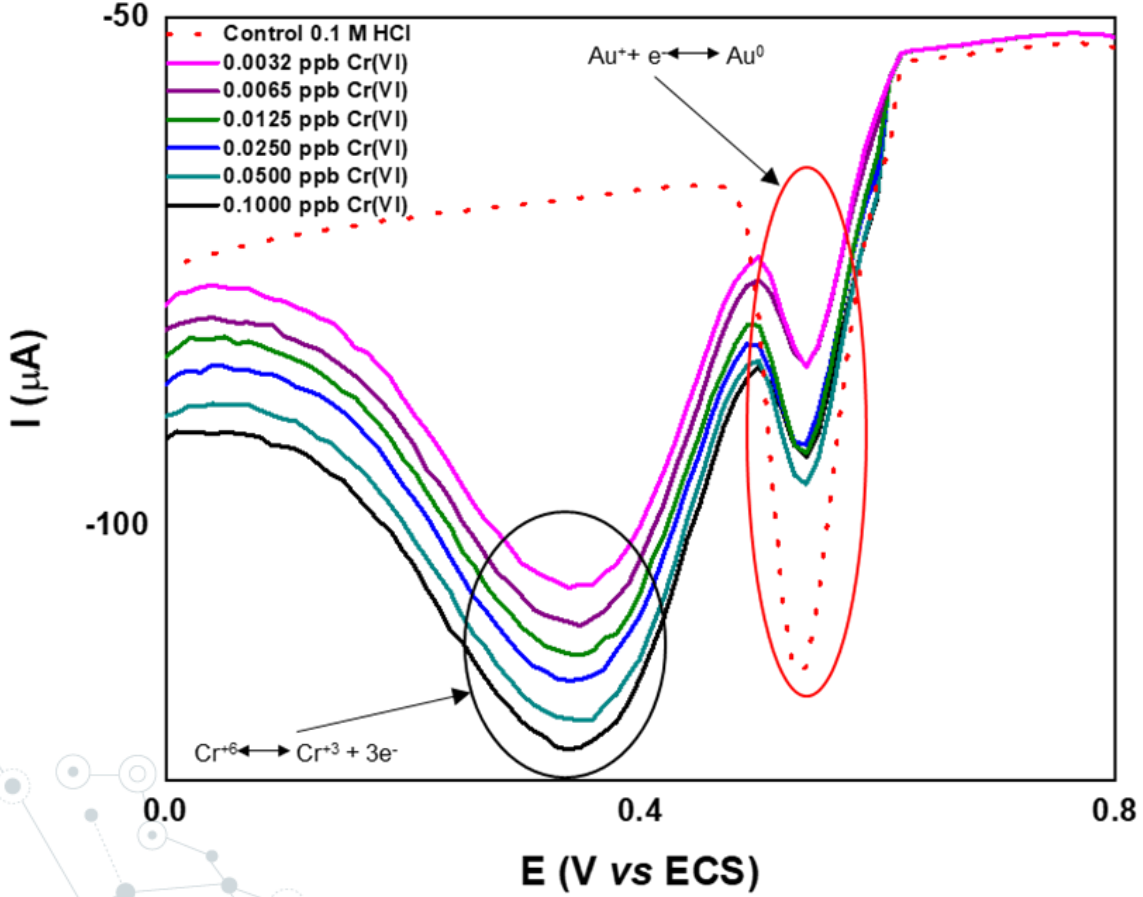
Supporting electrolyte: HCl 0.1 M

In **dot red line**

- a) MWCNT/CTS/GCE
- b)AgNPs/MWCNT/CTS/GCE
- c) AuNPs/MWCNT/CTS/GCE

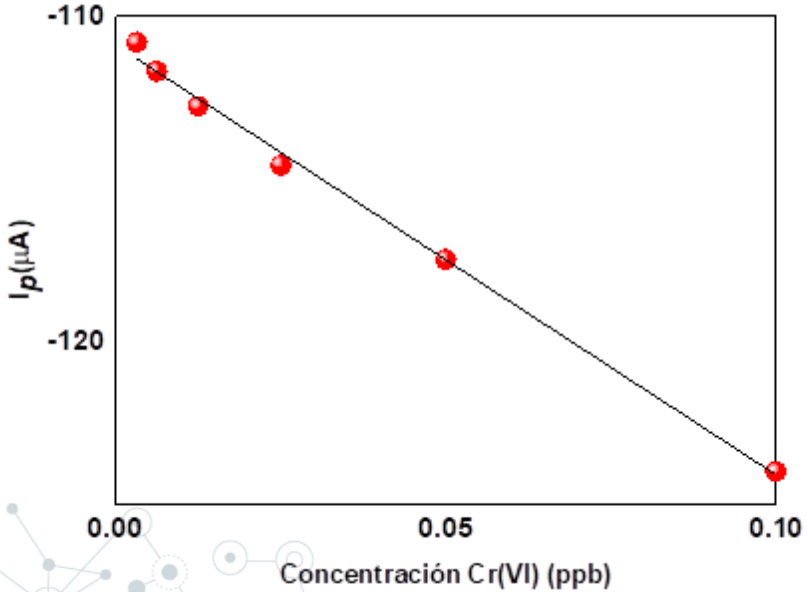
Diffetential Pulse Voltammetry onto AuNPs/MWCNT/CTS/GCE for Cr(VI)

Range: 0.003 a 0.1 µg·L^{-1}



Calibration plot obtained after optimization of parameters with DP Voltammetry for Cr(VI) in 0.1M HCl

Calibration Plot



Analytical Parameters

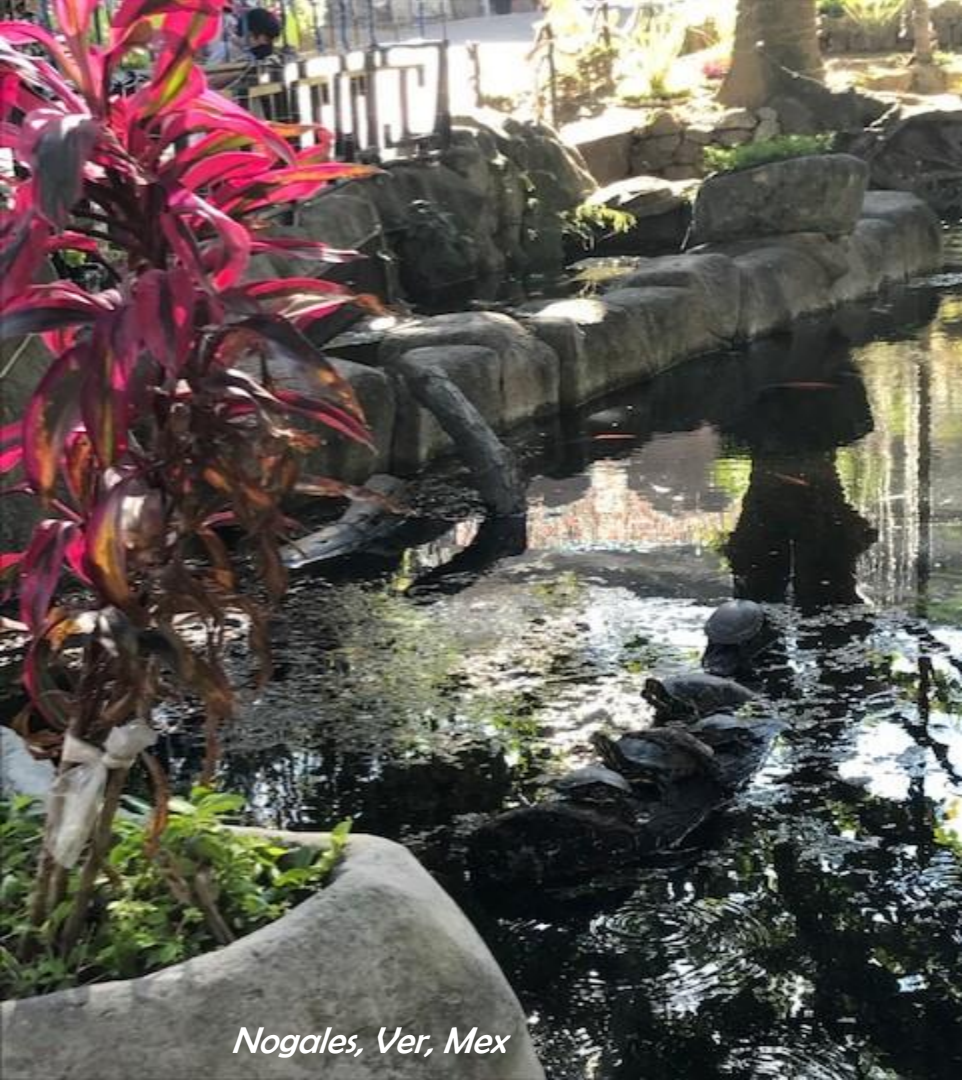
Parámetro	Valor optimizado
Linear interval (µg·L^{-1})	0.003 a 0.1
Regression analysis	y= -132.08x – 110.87 (r=0.998)
LOD (µg·L^{-1})	0.007
LOQ (µg·L^{-1})	0.020
Precision	0.020%
Accuracy	95.080%

Comparison of electrochemical sensors

Electrode	modification	technique	LOD (μgL^{-1})	Ref.
AuNPs/screen printed	Electrodeposition	DPV	7	Hilali, et. al. (2018)
AuNPs/**screen printed**	Electrodeposition	DPV	54	Hilali, et. al. (2018)
AuNPs/Nano-Tic/GCE	Electrodeposition	DPV	2.08	Ravi Shankar, et. al. (2015)
AuNPs/MWCNT/chit/GCE	**Chemically modified /Electrodeposition**	**DPV**	**0.007**	**This work**

Conclusions

- Electrodes modified only with MWCNT and Chit did not allow an electrochemical reduction of Cr(VI)
- The modified glassy carbon electrode with silver nanoparticles, multiwall carbon nanotubes and chitosan allowed a sensitive definition at 1 mg L-1
- This detection data obtained is acceptable for the official Mexican regulation 002 of the SEMARNAT that establishes the maximum permissible limits of Cr(VI) in wastewater.
- Detection limit of Cr(VI) at 0.007 µg·L-1 and a quantification limit of 0.02 µg·L-1, even in the presence of chloride anions
- Nanostructured electrochemical sensor fabricated in this work offers competitive application prospects for detection of Cr(VI) in aqueous medium.



Thank you for your attention

Questions?

Statistical Analysis

Electrochemical results of DPV at different Cr(VI) concentrations

Concentration Cr(VI) (μg·L^{-1})	ΔI (μA)		
	Repetition 1	Repetition 2	Repetition 3
0.1000	-123.98	-123.88	-124.05
0.0500	-117.75	-117.43	-117.19
0.0250	-114.78	-114.74	-114.17
0.0125	-112.80	-112.74	-112.73
0.0065	-111.47	-111.74	-111.82
0.0032	-110.78	-110.72	-110.87

Determination of Cr(VI) at 0.05 μg·L^{-1} byDPV

Concentración Cr(VI) (0.05 μg·L^{-1})	ΔI (μA)
Número de muestra	
1	117.47
2	117.46
3	117.49
4	117.42
5	117.49
6	117.46
7	117.45
8	117.45
9	117.42
10	117.40