Harnessing Chitosan Beads as an Immobilization Matrix for Zero-Valent Iron Nanoparticles for the Treatment of Cr(VI)-Contaminated Laboratory Residue

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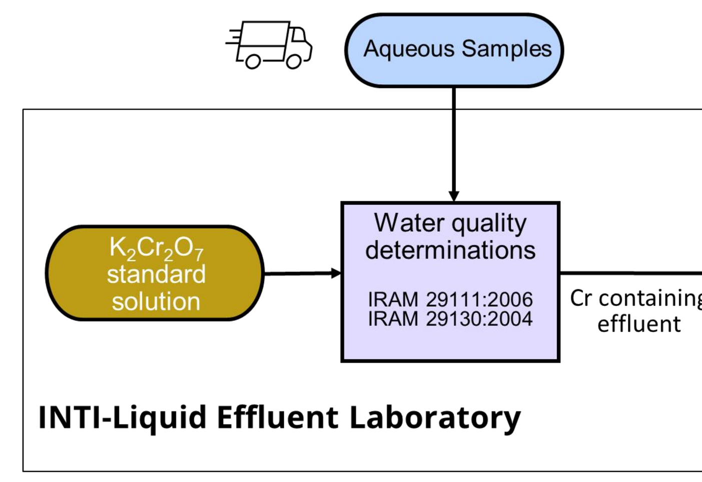
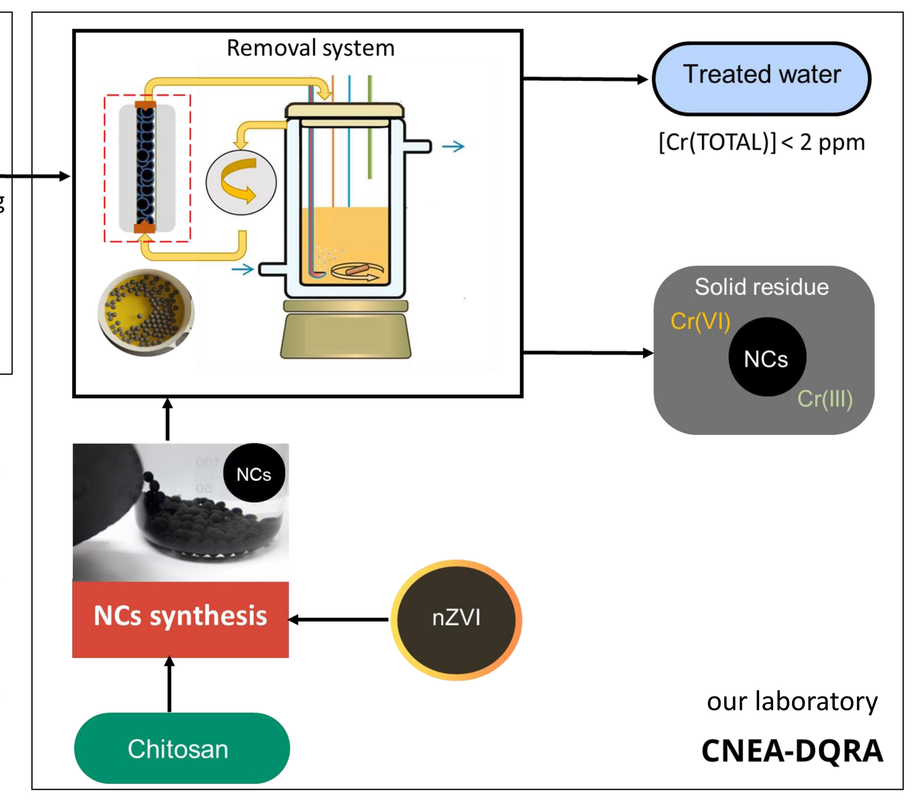
Introduction

The use of zerovalent iron nanoparticles (nZVI) immobilized in a chitosan (CS) polymer matrix is presented as an innovative and efficient solution for the removal of Cr(VI) in wastewater. nZVI, recognized for their high redox reactivity, have proven to be highly effective in removing various contaminants, including heavy metals. However, their tendency to agglomerate in aqueous media significantly reduces their surface area, reactivity, and mobility. To overcome these limitations, the formation of millimeter nanocomposites (NCs) by immobilizing nZVI is proposed, which facilitates their application in continuous flow systems as filling columns or reactive barriers. [1-2].



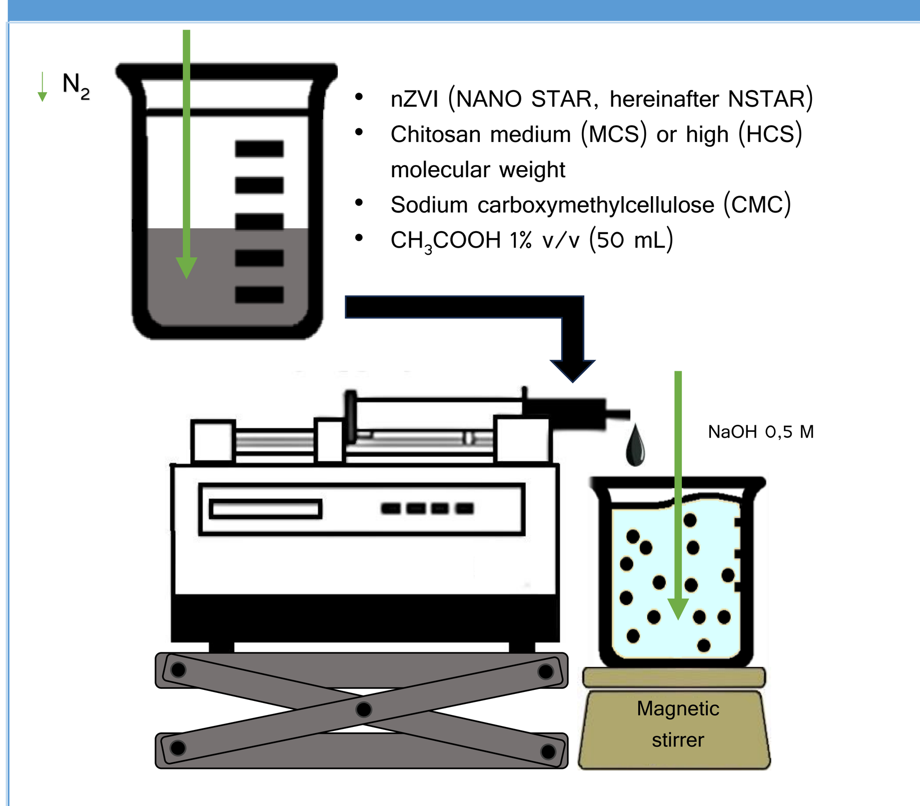


Usually, laboratory aqueous waste containing heavy metals are overlooked as target effluent for treatment before disposal of the dissolved solids, and particularly in Argentina, they are mandatory treated by incineration followed by disposal of the solid ashes.

The Liquid Effluent Laboratory of the National Institute of Industrial Technology (INTI) in Argentina produces 30 liters of liquid waste contaminated with Cr(VI) annually, the possibility of treating this wastewater internally becomes crucial.

The objective of this work was to develop an accessible and efficient treatment method that allows the reuse of wastewater generated in water quality analysis. To this end, the synthesis of NCs was optimized by exploring routes such as the prestabilization of nZVI with carboxymethylcellulose (CMC) and the use of CS with different molecular weights, obtaining materials with greater mechanical stability and reactivity. The characterization of the materials confirms their structure and stability, finally demonstrating that the NCs produced remove Cr(VI) from water to comply with water quality regulations and offer a cost-effective solution for the treatment of liquid waste contaminated with Cr(VI).

Synthesis and Characterization

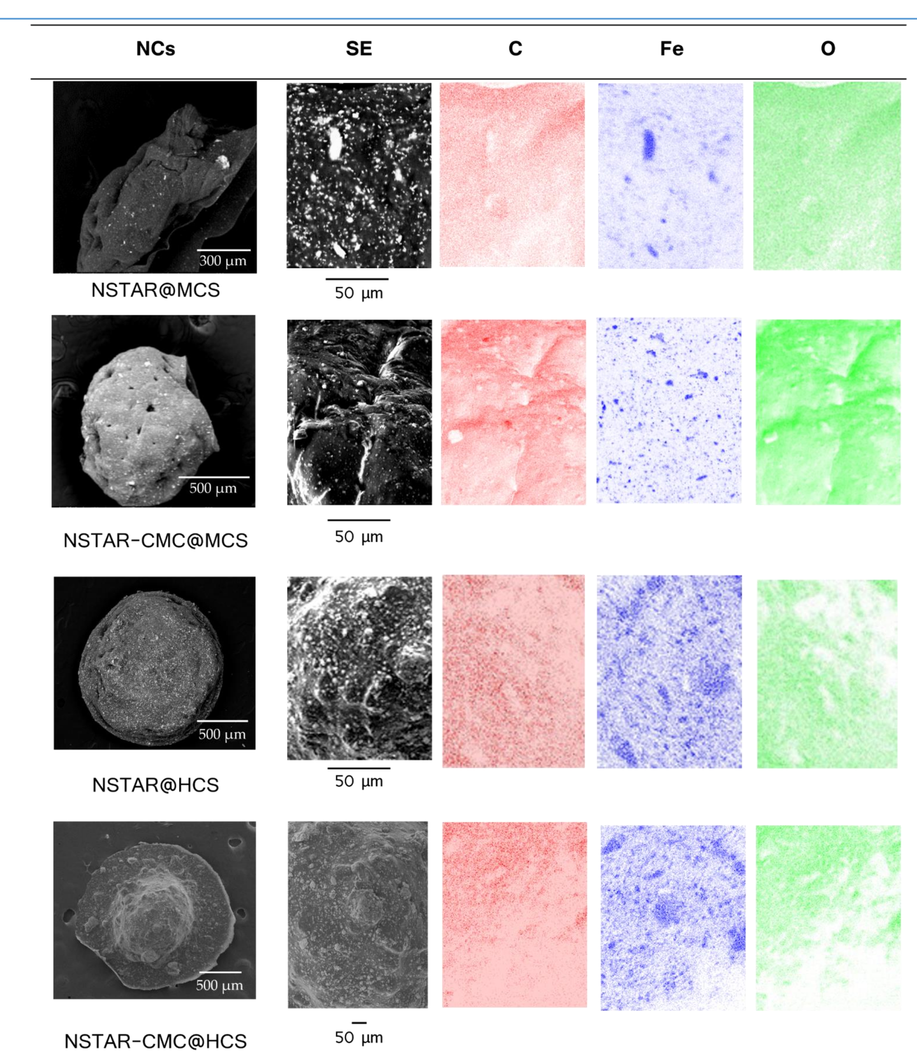


Setup of synthesis

Synthesized materials

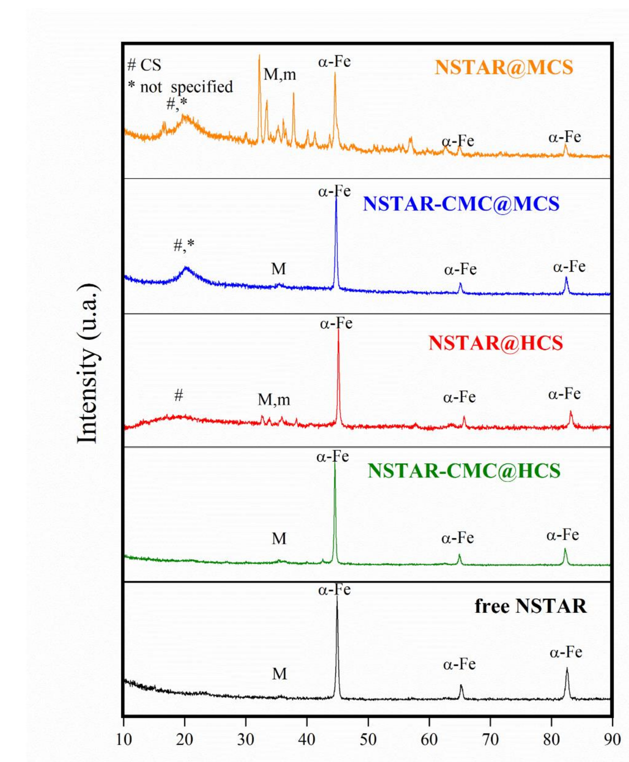
NCs	Beads of CS
NSTAR-CMC@MCS	HCS
NSTAR@HCS	CMC@MCS
NSTAR-CMC@HCS	CMC@HCS

SEM-EDS



SEM images of secondary electrons (SE) for NCs, including the distribution of C, Fe and O.

XRD



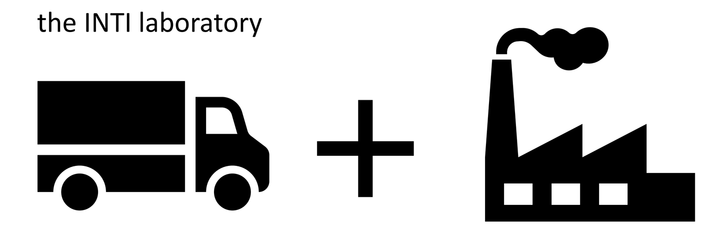
Diffraction spectra of NCs and free NSTAR. The peaks identified as #, M, m and * correspond to CS, magnetite, maghemite, and an unidentified substrate, respectively.

- **The NCs synthesized from MCS-CMC and QSA preserved the α-Fe phase as the dominant phase**, also allowing the identification of the presence of magnetite and/or maghemite that could not be differentiated. The use of HCS allows the α-Fe phase to be preserved without resorting to stabilization.

- **SEM-EDS revealed millimeter-sized spheres with micrometer-sized nZVI clusters randomly distributed**. Better nanoparticle dispersion was observed in NCs from the CMC-MCS and HCS combinations.

Treatment costs

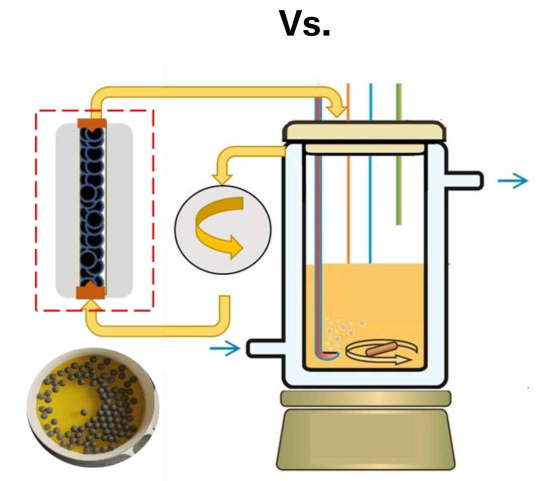
To treat 30 L of waste from the INTI laboratory



USD 319

(December 2023)

Vs.

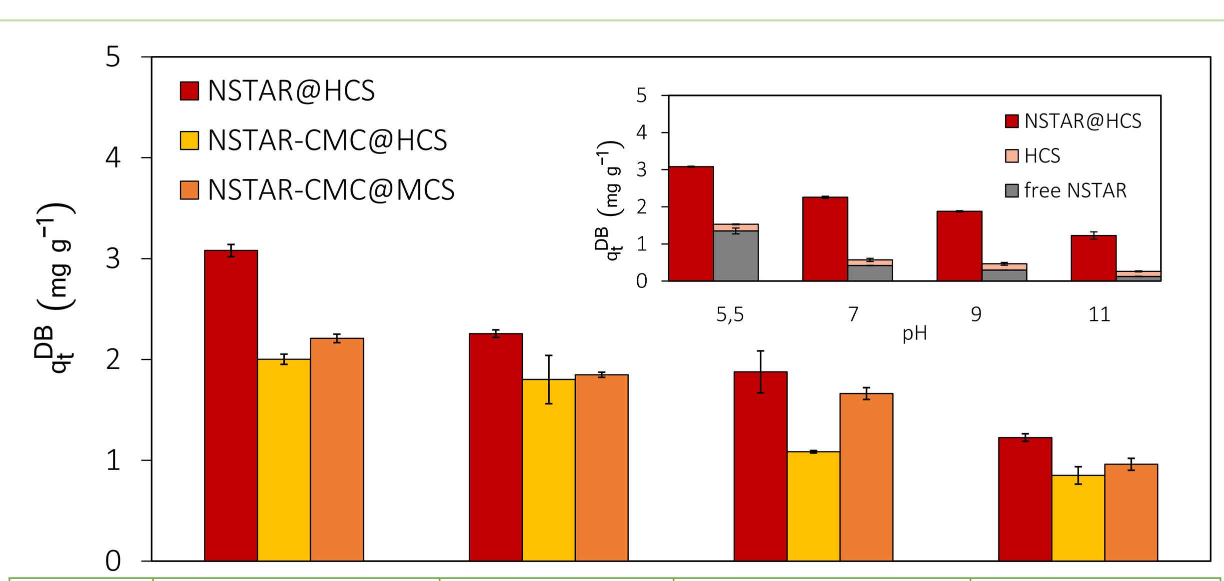


USD 72.1

- The total cost calculated is approximately three times lower than the cost quoted by an effluent treatment company offering waste transfer and treatment services to laboratories in Argentina.

Removal of Cr(VI)

pH and Immobilization and Type of NCs as Variables



Species/pH	5.5	7	9	11
Cr	$HCrO_4^-$ (-)	CrO_4^{2-} (-)		
CS	$-NH_3^+$ (+)	-NH_2NH		
CMC	-COOH	$-COO^-$ (-)		
NSTAR	$Fe(II,III)OH_2^+$ (+)		$Fe(II,III)O^-$ (-)	

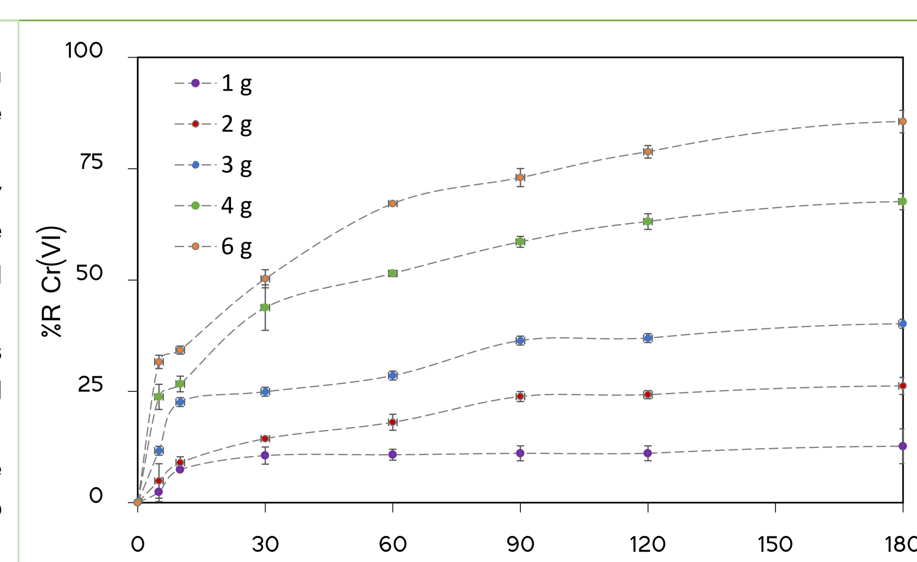
Cr(VI) q_t^{DB} removal capacity with NCs. Insert: q_t^{DB} obtained for NSTAR@HCS, HCS, and free NSTARs in solution. Initial conditions: synthetic water, $[Cr(VI)]_0$ = 65 μM, 0.7 g NCs, pHs: 5.5, 7, 9, and 11. Total time of the experiment, 2 h. Table: Cr(VI) species distribution and surface species of CS and nZVI as function of pH.

- **Cr(VI) removal increases with decreasing pH for the NCs and free NSTAR.**
- NSTAR (free or immobilized) efficiency increases with the charge difference between $HCrO_4^-$ and CrO_4^{2-} of Cr, and surface species of Fe.
- **The removal capacity of the NCs is higher than the sum of the removal capacities of CS and free NSTAR.**
- Only pH values of 5.5 or higher were used in the subsequent experiments to ensure higher removal efficiency.
- The removal capacity of Cr(VI) obtained with the NCs synthesized in this work is the highest, within the order of magnitude, of that found for similar materials based on iron nanoparticles (see table).

Cr(VI) removal efficiencies with NCs based on Fe-CS at different pHs obtained from bibliographic analysis.

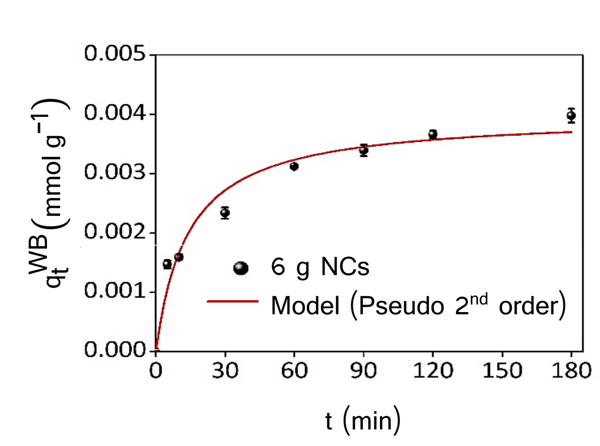
Material		pH	t (min)	q_t^{DB} (mg Cr(VI) g^{-1}FeNPs)
NPs	NCs			
comercial	nZVI@HCS (this work)	5.5	120	6.4
		7		4.7
comercial	nZVI@CS	6.4	40	1.6
comercial	nZVI@CS	3.9	60	4.0
comercial	nZVI@CS	3	60	6.0
Laboratory synthesized	IONPs@CS	6	480	4.4

Cr(VI) Removal in Real Water

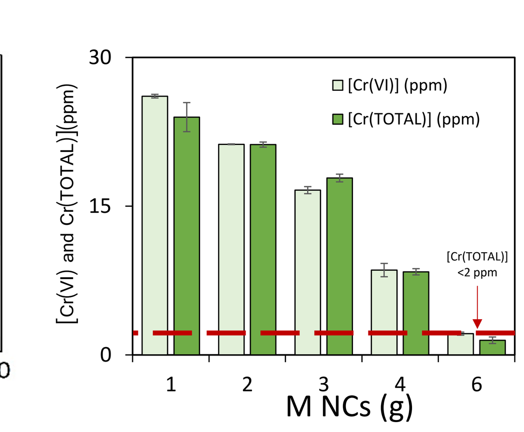


%RCr(VI) as a function of time for different masses of NSTAR@HCS tested.

- **The percentage of chromium removal increased in direct proportion to the mass of NSTAR@HCS added for each experiment.**
- **Using** 6 g of NSTAR@HCS, a final Cr(VI) concentration lower than the ACUMAR recommended value was achieved.



Kinetic fit of Pseudo 2nd order using 6 g of NCs.



Concentrations of Cr(VI) and Cr(TOTAL) obtained after 24 h for different masses of NCs.

- **Pseudo-second-order kinetic constants reported in literature are lower than those obtained in this study**. Other authors, using materials like those used here, reported kinetic constants between 10 and 100 times lower, which gives us the guideline that the removal system obtained is kinetically faster than that obtained by other authors [3,4], a vehement when it comes to removing Cr(VI).
- **Cr(VI) and Cr(TOTAL) concentrations found in solution were similar for all the NCs masses studied**, indicating that no Cr(III) was left in solution after contact with the NCs.

Conclusions

The NCs produced, consisting of NSTAR immobilized in CS, exhibited a stable structure and high efficiency in removing Cr(VI) from water. Various synthesis routes were explored, including the pre-stabilization of nZVI with CMC and the use of MCS and HCS. It was found that NCs formed millimeter-sized spheres with micrometer-sized aggregates of randomly distributed nZVI, and the α-Fe phase of nZVI was partially preserved after synthesis, predominating, especially in the NCs synthesized from CMC-MCS and HCS. The NCs proved to be highly efficient in removing Cr(VI), particularly in acidic environments, as expected. When tested on real effluents, the NCs effectively complied with both national and international regulation for Cr(TOTAL) limits. Additionally, they demonstrated a competitive cost when compared to outsourcing effluent treatment. These materials show promising potential for environmental remediation applications, both in synthetic waters and laboratory wastewater containing Cr(VI).

References

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