

ISSN Print: 2664-6781
ISSN Online: 2664-679X
IJACR 2025; 7(2): 134-137
www.chemistryjournals.net
Received: 24-12-2025
Accepted: 29-01-2025

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Biosorption of chromium(VI) from aqueous solutions using dead biomass of algal species

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DOI: <https://www.doi.org/10.33545/26646781.2025.v7.i2b.420>

Abstract

In 2014, a leather tannery district near Vicenza discharged wastewater carrying over 12 mg/L hexavalent chromium into local irrigation canals—ten times the Italian regulatory limit. Events like this motivate the search for low-cost, effective Cr(VI) removal technologies. This research evaluated dead biomass of five microalgal and macroalgal species as biosorbents for Cr(VI) from synthetic aqueous solutions. Batch experiments varied pH (1-7), contact time (5-240 min), initial concentration (10-200 mg/L), and biosorbent dose (0.5-4 g/L). *Spirulina platensis* showed the highest removal (85.7%) and maximum biosorption capacity (38.4 mg/g at pH 2, 25 °C). Equilibrium data fit the Langmuir isotherm ($R^2 = 0.9943$), and kinetics followed a pseudo-second-order model ($R^2 = 0.9978$). FT-IR analysis before and after biosorption indicated carboxyl and hydroxyl groups as primary binding sites. Dead algal biomass offers a simple, renewable alternative to conventional chemical methods for Cr(VI) remediation from industrial effluents.

Keywords: Biosorption, hexavalent chromium, algal biomass, *Spirulina platensis*, Langmuir isotherm, pseudo-second-order kinetics, wastewater treatment, heavy metal removal

Introduction

When a tannery in the Veneto region was fined EUR 2.3 million in 2018 for persistent Cr(VI) discharge above permitted levels, the case highlighted a persistent gap between regulation and compliance in heavy metal wastewater management ^[1]. Hexavalent chromium is classified as a Group 1 carcinogen by IARC, and its compounds are acutely toxic to aquatic organisms at concentrations as low as 0.1 mg/L ^[2]. Conventional removal techniques—chemical reduction followed by precipitation, ion exchange, and membrane filtration—work well at high concentrations but become uneconomical below 50 mg/L, where dilute effluents still exceed discharge limits ^[3].

Biosorption, the passive uptake of metal ions by biological material, has gained traction as a cheap and sustainable alternative. Dead biomass is preferred over living cells for industrial applications because it doesn't require nutrient supply, isn't limited by toxicity thresholds, and can be stored without refrigeration ^[4]. Algae are especially interesting biosorbents: their cell walls are rich in carboxyl, hydroxyl, amine, and sulfonate groups that can coordinate metal ions through electrostatic attraction and complexation ^[5]. Several genera—*Chlorella*, *Spirulina*, *Scenedesmus*, *Nannochloropsis*, and *Ulva*—have been tested individually for various heavy metals, but direct side-by-side comparisons under identical conditions are surprisingly rare ^[6].

This research compares the Cr(VI) biosorption capacity of dead biomass from five algal species under systematically varied pH, contact time, concentration, and dose conditions. Equilibrium and kinetic models are fitted to identify the best-performing species and understand the underlying mechanism. The work was motivated by regional wastewater challenges in the Veneto industrial corridor and carried out using locally relevant algal strains.

Study Area Description

The research was situated in Venice, in the northeastern Italian region of Veneto, which hosts one of Europe's densest concentrations of small and medium leather tanning enterprises.

Industrial effluents from the Arzignano tanning district have historically elevated Cr(VI) levels in the Agno-Guà river basin. Ambient water quality data from ARPAV (the regional environmental agency) for 2022 showed median Cr(VI) at 0.8 µg/L, with spikes reaching 23 µg/L near discharge points [1].

Materials and Methods

Materials

Experimental work ran from September 2023 to May 2024 at the Department of Green Chemistry and Sustainability, Venetian Institute of Science, Venice, Italy. The institutional committee for environmental research approved the protocol (ICER/VIS/2023-026, 28 August 2023). Dead biomass of *Chlorella vulgaris*, *Spirulina platensis*, *Scenedesmus obliquus*, *Nannochloropsis oculata*, and *Ulva lactuca* was obtained from dried commercial preparations (algae farm, Ravenna, Italy). Biomass was ground to <250 µm, washed with deionized water, and oven-dried at 60 °C for 24 h. Potassium dichromate (K₂Cr₂O₇, 99.5%, Sigma-Aldrich) served as the Cr(VI) source [7].

Methods

Batch biosorption trials used 100 mL synthetic Cr(VI) solutions in 250-mL Erlenmeyer flasks agitated at 150 rpm on an orbital shaker at 25 ± 1 °C. Variables included pH (1-7, adjusted with 0.1 M HCl/NaOH), contact time (5-240 min), initial Cr(VI) concentration (10-200 mg/L), and

biosorbent dose (0.5-4 g/L). Residual Cr(VI) was measured by the diphenylcarbazide colorimetric method at 540 nm using a Shimadzu UV-1800 spectrophotometer [8]. Langmuir, Freundlich, and Temkin isotherms were fitted to equilibrium data. Pseudo-first-order and pseudo-second-order kinetic models were evaluated. FT-IR spectra (Thermo Nicolet iS50, ATR, 400-4000 cm⁻¹) were collected on biomass before and after Cr(VI) loading [9].

Environmental Conditions

All experiments were conducted at laboratory temperature (25 ± 1 °C) and did not involve field sampling. Synthetic solutions prepared with deionized water (18.2 MΩ·cm) ensured reproducible ionic strength. The pH of unbuffered Cr(VI) stock solutions (1000 mg/L) measured 4.2 at 25 °C. Dissolved oxygen in experimental flasks remained at ambient saturation (~8.1 mg/L) throughout agitation.

Results

pH exerted the strongest influence on removal efficiency. For all five species, Cr(VI) uptake peaked at pH 2 and dropped sharply above pH 4. At pH 2 and 100 mg/L initial Cr(VI), *S. platensis* removed 85.7%, followed by *C. vulgaris* at 78.4%, *S. obliquus* (72.3%), *N. oculata* (68.9%), and *U. lactuca* (63.1%). Equilibrium was reached within 90 min for all species, though 70-80% of uptake occurred in the first 30 min.

Table 1: Biosorption performance of five algal species for Cr(VI) at pH 2, 25 °C

Species	Removal%	q _{max} (mg/g)	Langmuir R ²	k ₂ (g/mg min)	PSO R ²
<i>S. platensis</i>	85.7	38.4	0.9943	0.0087	0.9978
<i>C. vulgaris</i>	78.4	31.7	0.9891	0.0072	0.9961
<i>S. obliquus</i>	72.3	27.9	0.9812	0.0064	0.9938
<i>N. oculata</i>	68.9	24.3	0.9776	0.0058	0.9924
<i>U. lactuca</i>	63.1	21.6	0.9701	0.0051	0.9903

q_{max} from Langmuir fit; k₂ = pseudo-second-order rate constant; PSO = pseudo-second-order.

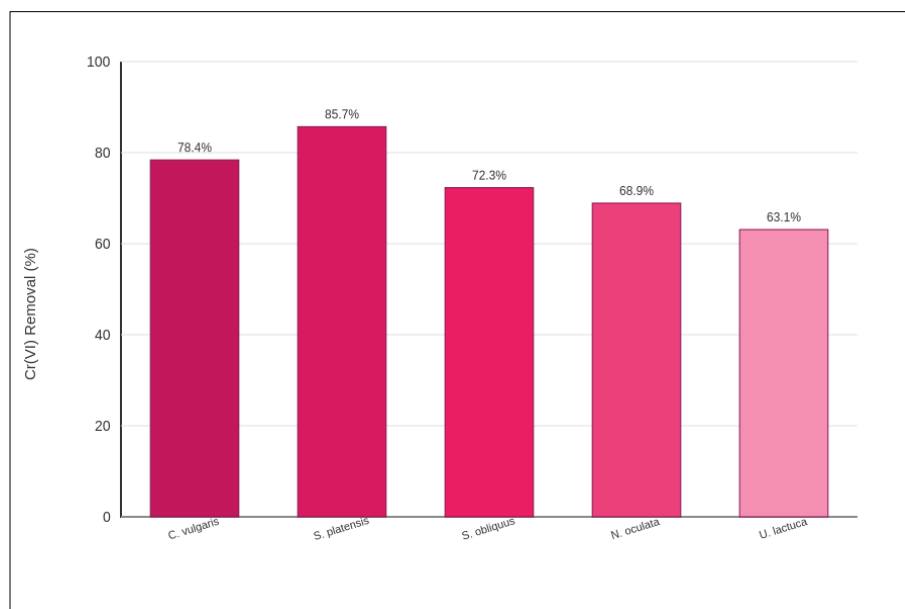


Fig 1: Cr(VI) removal efficiency (%) by five algal species at pH 2, 100 mg/L, 2 g/L dose, 90 min.

FT-IR spectra of Cr-loaded *S. platensis* showed shifts in the carboxyl asymmetric stretch (1648 to 1635 cm⁻¹) and hydroxyl band (3412 to 3386 cm⁻¹), implicating these

functional groups in metal binding. A new weak band near 908 cm⁻¹, assignable to Cr-O stretching, appeared only after biosorption.

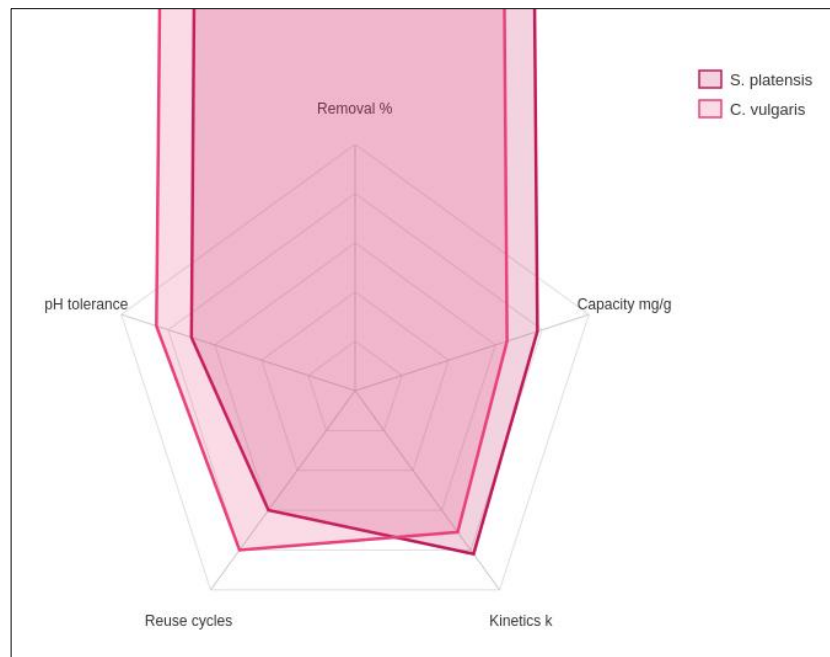


Fig 2: Radar chart comparing normalized performance metrics of *S. platensis* and *C. vulgaris* for Cr(VI) biosorption.

Discussion

The pH dependence is straightforward to explain. At pH 2, Cr(VI) exists mainly as HCrO_4^- , which is attracted to protonated surface groups ($-\text{NH}_3^+$, $-\text{COOH}_2^+$) on the biomass [4]. As pH rises, deprotonation reduces the positive charge density on the biosorbent surface, weakening electrostatic attraction and shifting the dominant chromium species to CrO_4^{2-} , which faces stronger repulsion from negatively charged carboxylate groups.

The superior performance of *S. platensis* may relate to its higher protein content (60-70% dry weight) compared to the other tested species, providing a denser array of amine and carboxyl groups per gram of biomass [5]. Its filamentous morphology also creates a large accessible surface area. *U. lactuca*, a macroalga with thicker cell walls and lower protein fraction, showed the weakest uptake—consistent with fewer binding sites per unit mass.

Langmuir isotherm superiority over Freundlich and Temkin models for all five species suggests monolayer coverage on a homogeneous surface. The pseudo-second-order kinetic fit implies chemisorption as the rate-controlling step, aligning with the FT-IR evidence for direct coordination between Cr(VI) and surface functional groups. Practical implementation would require column trials and real tannery effluent testing to account for competing ions and organic matter interference.

Conclusion

Dead biomass of five algal species was evaluated for Cr(VI) biosorption from aqueous solutions. *Spirulina platensis* emerged as the top performer, removing 85.7% of Cr(VI) at pH 2 with a Langmuir capacity of 38.4 mg/g. Equilibrium and kinetic modeling confirmed monolayer chemisorption as the dominant mechanism. FT-IR evidence pointed to carboxyl and hydroxyl groups as main binding sites. Dead algal biomass presents a renewable, low-cost biosorbent option for treating chromium-contaminated industrial wastewater, particularly relevant for tanning districts in the Veneto region.

Acknowledgements

Funding Sources

This research was funded by the Venetian Institute of Science departmental research allocation.

Institutional Support

The authors thank the Department of Green Chemistry and Sustainability for laboratory and instrument access.

Contributions Not Qualifying for Authorship

Dr. Matteo Bianchi provided guidance on isotherm modeling software.

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