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Removal of hexavalent chromium from electroplating wastewaters using marine macroalga *Pelvetia canaliculata* as natural electron donor

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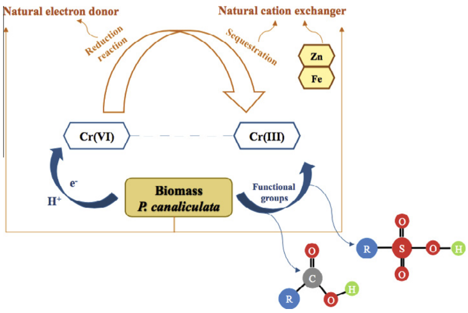
HIGHLIGHTS

- Treatment strategy for galvanic wastewaters containing Cr(VI), Cr(III), Zn and Fe.
- Macroalga *Pelvetia canaliculata* as a natural electron donor and cation exchanger.
- Cr(VI) is reduced to Cr(III) by contact with electron-donor groups of biomass.
- Sequestration of trivalent chromium, zinc and iron through cation exchange.
- Cr(VI) reduction using the biomass was performed in a packed bed column.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper reports a treatment strategy for an electroplating wastewater containing high amounts of hexavalent and trivalent chromium and zinc, and residual iron. The brown macroalga *Pelvetia canaliculata* was used as a natural electron donor for the reduction of Cr(VI) to Cr(III) at acidic pH, and as a natural cation exchanger for zinc, iron and trivalent chromium sequestration. The strategy adopted for the wastewater treatment involves: (i) the reduction of Cr(VI) to Cr(III) using the macroalga as electron donor; (ii) trivalent chromium, zinc and iron precipitation at pH 8.5; and (iii) the removal of residual zinc ions (13 mg/L) by cation exchange at pH 8.5, using the negatively charged functional groups present at the surface of *P. canaliculata*.

The Cr(VI) reduction was evaluated as a function of the biomass and Cr(VI) concentration, pH and temperature. The reaction was promoted through biomass oxidation in acidic medium. The Cr(VI) reduction capacities of raw and protonated *P. canaliculata* were around 1.8 and 2.3 mmol/g and the values for the Cr(III) uptake capacity of the oxidized biomass were 0.8 and 1.9 mmol/g, respectively. The results suggest that the oxidation of the biomass during Cr(VI) reduction generates new negatively charged active sites for cation binding. The continuous treatment of the wastewater containing Cr(VI) was evaluated in a column packed with raw *P. canaliculata*, and a maximum Cr(VI) reduction capacity of around 2.1 mmol/g was achieved. After the Cr(VI) removal step, 100% (below the detection limit) and 95% of the remaining trivalent chromium and zinc, respectively, can be eliminated by precipitation at pH 8.5.

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Nomenclature

a	empirical constant
A	Arrhenius's frequency factor
$[B]$	biomass concentration (g/L)
C	concentration of metal species in the liquid phase (mmol/L)
C_0	initial concentration of metal species in the liquid phase (mmol/L)
C^*_{OC}	content of organic compound equivalent per unit gram of biomaterial (mmol/g)
$[C(VI)]_t$	hexavalent chromium concentration in the liquid phase at time t (mmol/L)
$[C(VI)]_0$	initial hexavalent chromium concentration in the liquid phase (mmol/L)
$[C(III)]_0$	initial trivalent chromium concentration in the liquid phase (mmol/L)
E_a	activation energy (J/mol)
k	rate coefficient of hexavalent chromium reduction kinetic (L/mmol/h)
L	bed length (cm)
n	order of reaction with respect to proton concentration
pH_i	initial pH
pH_f	final pH
q	metal concentration in the solid phase (mmol/g)
Q	flow rate (mL/min)
R	gas constant (8.314 J/mol/K)
R^2	correlation coefficient
S_R^2	model residual variance $(mmol/g)^2$
t	time (s)
T	solution temperature (K)
τ	space time (min)

1. Introduction

The dumping of toxic pollutants, such as heavy metals (Cr, Zn, Fe and Ni) [1], into water bodies could harm aquatic life and as result, natural waters can be unsuitable as a source of safe drinking water [2]. Electroplating is a branch of the metalwork industry in which the treatment of metal surfaces is carried out through chemical and/or electrochemical processes. The galvanizing process involves a sequence of pretreatment, coating and surface conversion baths. These procedures lead to the generation of several types of wastewaters containing high amounts of metals, principally zinc, iron and hexavalent chromium [1,3,4].

Zinc and iron are essential elements for living beings, but in high concentrations they become toxic. Hexavalent chromium is a carcinogenic and mutagenic agent which can cause damage to the kidneys and lungs as well as skin ulcerations [5–7]. Trivalent chromium is around 300 times less toxic and less water-soluble and mobile than the hexavalent form.

In general, the treatment of galvanic wastewaters containing hexavalent chromium involves the following steps [2,8,9]: (i) reduction of Cr(VI) to Cr(III) under acidic conditions (pH between 2 and 3) through the addition of ferric chloride ($FeCl_2$), sodium sulfide (Na_2S) or sodium bisulfite ($NaHSO_3$); (ii) oxidation of Fe(II) to Fe(III) with H_2O_2, (iii) precipitation of metals through the addition of hydroxides (pH ~ 7.0–8.5); (iv) flocculation to destabilize colloids through the addition of a polyelectrolyte (generally, anionic polyelectrolyte); and finally (v) sludge thickening and dewatering. However, in conventional treatments, the reduction of Cr(VI) may be incomplete and the chemicals used are hazardous to the environment besides being costly [10]. Chemical precipitation is not usually sufficient for the removal of the entire pollution load and the effluents discharged into the environment can be toxic. In addition, this procedure leads to the production of a solid residue. According to the European Waste Catalogue this residue belongs to the CER 19 02 group and according to the Brazilian norm NBR 10.004 it belongs to Class I, that is, it is classified as a hazardous and toxic waste. The safe disposal of this sludge is usually associated with high costs [1,11,12]; however, the reuse of the sludge from the electroplating industry is a promising alternative. Galvanic sludge (e.g., chromium, aluminum, zinc and ferrous sediment) can be applied in the production of ceramic pigments [13]. Several researchers have suggested alternatives for the reuse of the $Cr(OH)_3$ precipitate (e.g. as a precursor for ceramic pigments, generating chemicals for use in the tanning process), turning it into a raw material for other processes [14–16].

The use of biomass which is available in abundance worldwide, such as algae or residues from industrial operations, has been widely investigated for the sequestration of metal ions from aqueous solutions [2,17]. This process offers advantages such as low operation cost, the possibility of metal recovery, biomass regeneration and the minimization of the volume of chemical sludge generated. It has been reported that Cr(VI) can be reduced to Cr(III) in aqueous solutions using various marine macroalgae, especially under acidic conditions, where the biomass provides the electrons required for the reduction reaction [10,18–22].

Due to the potential environmental risk of the electroplating industry effluents, this study evaluated the employment of treatment technologies to minimize the generation of industrial waste and the use of chemicals, in order to achieve a final effluent with a low residual content of heavy metals. Thus, a treatment strategy for electroplating wastewater containing high amounts of hexavalent chromium, trivalent chromium, zinc and iron, combining oxidation/reduction reactions, precipitation and ion-exchange processes, is proposed. Several macroalgae were applied as a natural electron donor for the reduction of hexavalent chromium to its trivalent state. The raw and protonated forms of the macroalga *Pelvetia canaliculata* were selected for a more detailed study regarding the main factors affecting the Cr(VI) reduction kinetics. A final wastewater polishing step, after the Cr(VI) reduction and the chemical precipitation of trivalent chromium, zinc and iron, was evaluated using the brown macroalga *P. canaliculata* as a natural cation exchanger.

2. Experimental methods

2.1. Biomass

The use of different macroalgal species was investigated in this study: *P. canaliculata* and *Laminaria digitata* (brown algae) were collected from a coastal region in northern Portugal; *Sargassum cymosum* (brown alga) was collected from a coastal region in southern Brazil; *Gracilaria cervicornis* and *Gracilaria caudata* (red alga) were collected from a coastal region in the northeast of Brazil; and *Gracilaria birdiae* (red alga) and *Arribadas*, both originating from a coastal region in Ceará Stage, Brazil, were purchased from the Association of Algae Producers of Flecheiras and Guariju (APAFG). The seaweed samples were firstly washed with tap water and then distilled water to remove sand and excess salts, oven dried at 45 °C overnight. The *P. canaliculata* and *S. cymosum* algaes were crushed in a mill (Retsch, ZM 100), sieved (Retsch, AS 200) to