A new technology for the treatment of chromium electroplating wastewater based on biosorption

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ABSTRACT

In this work, an electroplating wastewater treatment based on biosorption followed by flocculation/precipitation is proposed. Biosorption was carried out by using exhausted coffee which has proved to be an efficient low cost sorbent for metal ions and reducing agent of hexavalent chromium in our previous works. After biosorption Cr(VI) concentration in the effluent met the wastewater treatment plant discharge regulation limit for hexavalent chromium ($0.5\,mg\,L^{-1}$). The addition of a suitable concentration of coagulant/flocculant resulted in the precipitation of residual trivalent chromium and other metal ions. The high correlation coefficients between Cr(VI) and Cr(III) and conductivity and pH values measured during the biosorption process highlighted the possible use of these two parameters to monitor the process. Indeed, these two parameters measured online resulted to be effective indicators of both process development and the end point of the process.

The merits of the proposed treatment which are considered over other techniques are much lower electrical energy consumption; less amount of chemicals addition and the possibility of chromium recovery from the sorbent at a quite high level of purity. Moreover, biosorption is an eco-friendly process and implies the reuse of a product at the end of its useful life rather than being disposed in landfill.

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1. Introduction

Electroplating is one of the varieties of several techniques of metal finishing. It consists on the deposition of a fine layer of one metal on another metal or material through electrolytic process to provide the surface of the manufactured product with various properties and attributes, such as corrosion protection, enhanced surface hardness, lustre, colour, aesthetics and value addition [1]. Typical plating includes brass, bronze, cadmium, copper, chromium, iron, lead, nickel, tin and zinc, as well as some precious metals such as gold, platinum and silver [2]. The method is simple and inexpensive and is used in different fields such as the automobile industry, electronics, optics, etc.

Electroplating is among the industries in which chromium is used widely. Chrome plating can be achieved by using salts of both trivalent and hexavalent chromium oxidation states. The main component in hard chrome plating solution is chromic oxide (CrO_3) dissolved in water [3]. Wastewaters generated in washing and rinsing operations of the plating process contain high concentrations of Cr(VI) and low concentrations of soluble forms of various metal salts at low pH (3–5). Due to its high toxicity Cr(VI) must be removed or reduced to Cr(III) in order to meet the permissible limits to discharge.

Reduction of Cr(VI) in acid solutions can be attained by using chemical reducing agents such as sulphur compounds (sulphur dioxide, sodium bisulfite or sodium met-bisulfite) and iron salts (ferrous sulphate) [4]. Electrochemical methods are also used in industrial wastewater treatment plants to reduce hexavalent chromium because of the use versatility of this kind of methods. Among electrochemical methods, electrocoagulation by using either iron and aluminium electrodes, electrodissolution of iron and different kind of electrodes (carbon and graphite, conducting polymers and copper) are used for Cr(VI) reduction [5,6].

Removal of Cr(VI) can be achieved by adsorption using ion exchange resins or granular activated carbon [7]. However, these methods are costly, the sorbents must be regenerated, which increase the cost of the process and sometimes the procedures are inconvenient [8]. Thus, during the last two decades, the aim of researchers dealing with sorption was to explore new and low cost sorbents for metal ions sorption. Cr(VI) removal by sorption onto

different types of biomass has been investigated [9–13]. Numerous studies show the capacity of bacteria [14–16], fungi, yeast [17], lignocellulosic materials [18], agro-food wastes [19–26] among other biosorbents to reduce Cr(VI) from synthetic solutions and wastewater. Biosorption using low-cost adsorbents was considered one of the promising techniques to treat chromium contaminated waters. Several studies using biomass to sorb Cr(VI) and to reduce it to its trivalent form from wastewater have been undertaken [1,27,28]. Nevertheless, the application of a biosorption technique has not had much success among the personnel responsible of the wastewater treatment. Among other disadvantages they argue that homogeneity of the material and its availability in large quantities and at any time are not assured. Up to our knowledge none of these attempts have yet been implemented in an industrial wastewater treatment plant and most of these residues remain unutilized being discharged to the environment where they cause severe contamination and environmental pollution problems due the toxic nature (presence of caffeine, tannins, and polyphenols) [29].

Coffee is the world second most popular beverage after water. Coffee silverskin and spent coffee grounds are the main coffee industry residues [30]. The exhausted ground coffee waste used in this study is generated in a soluble coffee industry that processes 50.000 t of coffee grounds per year. Tokimoto et al. [31] reported a worldwide annual generation of 6 million tons of soluble coffee. These data reflect the magnitude of residues generated by soluble coffee industry and the problems related to their disposal due to the toxic nature of these wastes. Exhausted coffee has proved to be an efficient sorbent for the removal of Cr(VI) from both single solutions [32–34] and binary mixtures with divalent metals [35].

Traditional plating wastewater treatments include two main steps: Cr(VI) reduction and precipitation of Cr(III) and other metal ions as hydroxides. In this work, a biosorption reactor replaces the unit in which Cr(VI) reduction is achieved by using different hexavalent reducing methods. The reactor is integrated in the treatment plant as a first step of the wastewater treatment, the second step being precipitation by alkalinisation of the solution and further addition of coagulant/flocculant.

2. Experimental

2.1. Materials

Exhausted coffee (EC) was kindly supplied by a soluble coffee manufacturer from Catalonia region, Spain. The waste was first dried in an oven at $105\,^{\circ}$C until constant weight and then sieved to collect the particle size of 0.5-1.0 mm. Hexavalent chromium and copper solutions were prepared by dissolving appropriate amounts of $K_2Cr_2O_7$ (s) from Scharlau and $CuCl_2 \cdot 2H_2O$ (s) from Merck in Milli-Q water, respectively. HCl solution (Fluka) was used to adjust the initial pH to pH 2.0. 1,5-Dyphenilcarbazide (Panreac), ethanol (Scharlau) and H_2SO_4 (Scharlau) were used for Cr(VI) analysis by Sequential Injection Analysis (SIA). Chromium, divalent and trivalent metals standard solutions $(1000\,mg\,L^{-1})$ purchased from Panreac were used for flame atomic absorption (FAAS) calibrations. All reagents used were of analytical grade.

2.2. Industrial wastewater

Industrial effluents were supplied by a chrome plating facility in Catalonia region (Spain) that generates a waste stream containing primarily high Cr(VI) concentration. Samples were stored in the dark in a cold room at $4\,^{\circ}$C.

Samples of electroplating wastewaters from rinsing baths (E1–E3) were taken for three consecutive days. Results of characterisation of the three diluted (1:3) wastewaters were carried

Table 1
Electroplating effluents characterisation.

Properties	E1	E2	E3
Metal $(mg\,L^{-1})$			
Cr(VI)	112.49	108.50	147.18
Cr(III)	0.00	0.00	0.00
Cu	5.04	8.20	8.01
Ni	1.04	0.93	1.23
Fe	4.24	8.54	5.51
Al	0.90	0.66	0.99
Anions $(mg\,L^{-1})$			
SO_4^{2-}	93.84	98.81	132.49
PO_4^{3-}	n.d.[a]	n.d.[a]	n.d.[a]
Conductivity $(mS\,cm^{-1})$	3.46	3.38	3.29
pH	3.02	3.05	3.01
ST[b] $(mg\,L^{-1})$	677	653	820
SS[c] $(mg\,L^{-1})$	16	17	19

[a] Not detected.
[b] ST: Total suspended solids.
[c] SS: Suspended solids.

out at the laboratory of Water Analysis of the Chemical Engineering department of our university and are presented in Table 1. As seen in Table 1 the three electroplating effluents mainly contain Cr(VI) with low concentrations of some divalent and trivalent metals. For biosorption experiments the pH of the industrial effluents was adjusted at pH 2.0.

2.3. Biosorption set-up

The biosorption set-up is shown in Fig. 1. A glass reactor of 10 L provided with a bottom drain valve was used in biosorption experiments. An agitator paddle ensured the homogeneous dispersion of the sorbent in the solution. Sampling was performed via an automatic sampling system (AS) recently developed in our group. A peristaltic pump (Gilson, Minipuls 3) and a fraction collector (Gilson, FC203B) were programmed to take 7 mL of sample at predetermined intervals of time. The bottom of the sampling tube was covered with glass wool, acting as a filter in order to prevent EC particles reaching and damaging the 3-way valve of the fraction collector. A recirculation system was adapted to return the excess of sampled solution volume or when the auto sampler was inactive. Monitoring of wastewater conductivity and pH during the biosorption process was performed by means of a portable multiparameter probe (HANNA HI9828).

2.4. Biosorption process

Biosorption experiments were carried out by putting into contact 53.33 g of EC of particle size (0.5–1.0 mm) with 8 L of wastewater samples (E1–E3) in a 10 L batch reactor under continuous agitation (350 ppm) at room temperature $(20 \pm 2\,^{\circ}$C). The sorbent dose $(6.67\,g\,L^{-1})$ resulted to be the most efficient in a previous work [36]. During the first half an hour, sampling was frequently done (every 5 min) so as to get as much as possible information about the sorption rate at the beginning of the process. Experiments lasted within the interval of 72–168 h. Once the biosorption process was stopped, both EC particles and bisorption treated water were drained through the drain valve in the bottom of the reactor. Solid particles were separated by filtration and the treated wastewater was stored until it underwent flocculation/precipitation treatment.

2.5. Flocculation/precipitation

Alkalinisation of the pH and the addition of a coagulant/flocculant such as an inorganic salt or a polymer create a solid