



## A comparative evaluation of biological activated carbon and activated sludge processes for the treatment of tannery wastewater



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### ABSTRACT

Depuration methods usually adopted to treat the tanning industry wastewater are based on several technologies, physicochemical or biological, as activated sludge (AS), alone or combined. The AS method faces some difficulties when pollutants toxic are present in the wastewater. The water treatment known as the biological activated carbon (BAC) allows overcoming these limitations by taking advantage of the synergism between activated carbon (AC) and microbacteria. Nevertheless, further investigation about the performance of BAC on real wastewater is much required. For this purpose, an experimental test with BAC in continuous pilot plant with a real tannery wastewater was performed. The same test was performed with AS process and relevant differences from BAC method were observed. The experimental results indicate the good removal of total chromium for both BAC and AS (72–70%). But the main differences are for soluble chromium removal (67% for BAC and 46% for AS) and for COD removal (66% for BAC and 40% for AS). Very good results were also obtained for removal of other pollutants resulting from industrial additives, for BAC (91–100%) and to a lesser extent for AS (28–78%). In every case, the BAC shows faster kinetics removal. Finally, a pseudo-second order model fits the experimental data about soluble chromium.

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### Introduction

The tanning industry has a deep impact on the environment because it generates high amount of wastewater which contains dangerous pollutants such as chromium which is considered one of the most toxic metals by the World Health Organization [1]. Albeit in the tannery industry the chromium is used as trivalent form, Cr(III), which is less dangerous than the hexavalent form Cr(VI), toxicological studies report that the trivalent chromium compounds could cause skeletal and neurological disorders [2].

Depuration technologies usually adopted to treat industrial wastewaters include precipitation, membrane filtration, adsorption, ion exchange, advanced oxidation, and biological processes [3–10]. The utilization of AS presents some difficulties because the heavy metals inhibits the biological processes [11,12]. These difficulties are usually overcome by adopting some of the abovementioned methods, combined or as pre-treatments. Among them, AC adsorption seems to be an attractive choice [3,13]. In fact,

the addition of granular activated carbon directly into the biological plant for wastewater treatment has been investigated as a suitable and less expensive technique to improve the treatment performance [13,14].

Uptake of the metallic ions on carbons mainly depends on the ions concentration and on adsorption capacity, which is linked to functional groups present on the carbon surface [15,16]. The concentration of ionic species in solution represents the driving force for mass transport to carbon surface. The presence of acid and basic functional groups on the surface of carbons assures that these materials are able to capture metallic ions [15,17–19]. These phenomena are strongly related to the pH of the solution.

The biotechnological method for water treatment known as BAC exploits the bacterial activity on activated carbon particles so that the removal of pollutants utilizes the combination of adsorption and biodegradation techniques [20–23]. The rough porous surfaces of the AC particles are suitable for microbial colonization that grow and form a layer of biomass, called "biofilm" [20]. The use of a support provides the necessary surface for the development of biofilm structures. These biofilm structures are composed by exo-polysaccharides, known as EPS (extracellular polymeric substances), produced by the bacteria, consisting of carbohydrates, proteins and abiotic components. In addition, the

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biofilms provide high biomass concentration per unit volume and allow the bacteria to adjust to the environmental conditions [20]. The biofilm, in addition to the capacity to biodegrade, a significant fraction of dissolved organic matter [21] is capable to capture the metal ions through many ways; among which the physicochemical interaction between the metal and functional groups of the EPS is the most common [24–27].

The performance of BAC is influenced by different parameters such as type of activated carbon, bacterial consortium and physicochemical characteristics of the wastewater [20]. The studies of the BAC treatment for pollutant removal commonly involve aqueous model or synthetic wastewater with removal efficiencies of chromium higher than 90% and that of organic carbon up to 75% [21–24]. Therefore, there is a lack of information about the performance of BAC method for real tannery wastewater treatment. In this study, the effects of BAC process on the various pollutants (inorganic and organic) contained in the tannery wastewater were investigated. We used granular commercially activated carbon Filtrasorb 400 [28,29] after characterization through adsorption tests. In order to evaluate the difference between the BAC method and a conventional biological process, the wastewater was treated in parallel by AS process. Although the study will evaluate the impact of processes on removal of TSS, COD, TOC and chemical additives, the main emphasis will be placed on the impact in removing chromium (total and soluble) since chromium is the main hazardous pollutant. A pseudo-second order model was used to fit the experimental data about soluble chromium concentrations measured after BAC and AS treatments.

## Materials and methods

### Experimental equipment

The experimental activities were performed in two similar pilot scale plants operating separately with BAC and AS technologies. The plants were located in the Research Center of Portici laboratories, making the activities independent from the seasons or weather conditions. In Fig. 1, the experimental apparatus is being illustrated.

The two plants work in parallel on two flows of same wastewater (Fig. 1a). Two tanks ( $T_1$ ,  $T_2$ ), each of  $1\text{ m}^3$ , were utilized

for storage of the wastewater and of the treated water respectively. The first tank ( $T_1$ ) was stirred; in this way, the sedimentation of insoluble components was avoided.

Each plant (Fig. 1b) was composed by a reactor and a clarifier-settler, with volume of 40 and 30 L, respectively; the pipeline was in stainless steel 316. The reactors were provided with temperature, pH and oxygen probes, for continuous and remote measurement. The AS reactor was also equipped with a suspended solid probe. Each reactor was stirred and a micro diffusor, placed in the bottom, insufflate air. The airflow rate was measured by float gauges ( $F_2$ ). The liquid flow rates were measured continuously by an electromagnetic system ( $F_1$ ,  $F_3$ ) and also monitored remotely.

In Table 1, the main operating conditions of the pilot scale plants for the experimental test which were optimized through a preliminary test [30] are being reported.

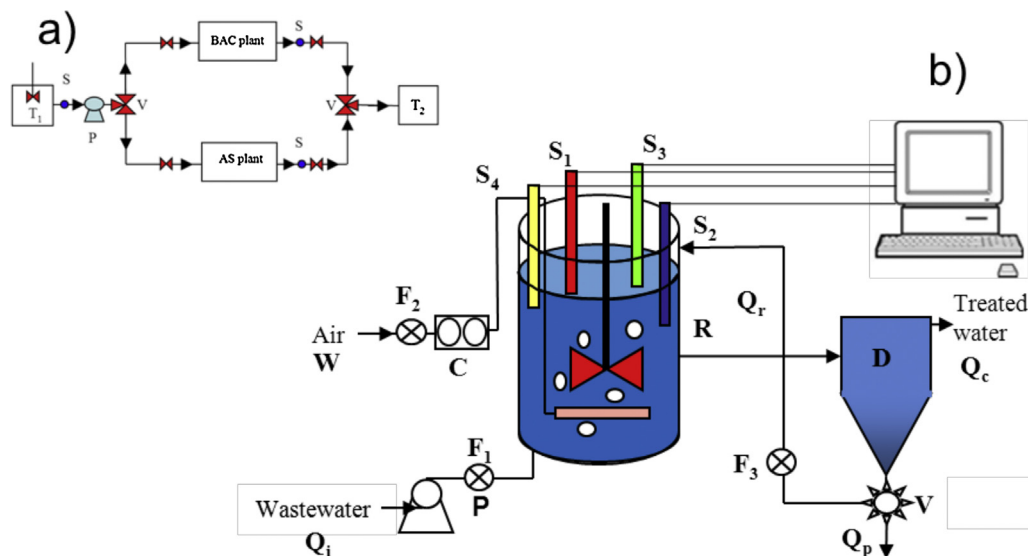
The feed flow for each line is slightly variable due to the use of peristaltic pump.

### Analysis

The concentration of chromium was measured by inductively coupled plasma mass spectrometry (ICP-MS) model ELAN 6000 PerkinElmer Inc. equipped with a cross-flow nebulizer.

Soluble chromium was determined in the wastewater, before and after treatment, after filtration with a  $0.45\text{ }\mu\text{m}$  membrane in order to remove the insoluble chromium fraction and analyzed without any further treatment. The total chromium concentration in the wastewater, before and after treatments, and in the sludge formed at end of test, was determined in acid digested extracts of unfiltered samples of wastewater and sludge, respectively. These samples (2 mL for the unfiltered wastewater; 0.25 g for the sludge) were processed at microwave digestion using a Multiwave Anton Paar GmbH with acidic solution containing 5 mL  $\text{HNO}_3$  concentrated 67% (super pure grade Romil Ltd.) and 2 mL  $\text{H}_2\text{O}_2$  (superpure grade Aristar BDH) in a closed teflon vessel. The digestion program was done in following way: at 250 W over 5 min, 400 W over 10 min, 600 W over 10 min and 250 W 5 min. After digestion, the solutions were analyzed for chromium by ICP-MS.

The operating conditions for measurements of chromium were ICPRF power 1000 W, nebulizer Argon 0.9 mL/min, isotopes analyzed  $\text{Cr}^{50}$ ,  $\text{Cr}^{52}$ , and  $\text{Cr}^{53}$ ; data acquisition took place by



**Fig. 1.** Experimental equipment. (a) Flow chart of the plants.  $T_1$ : feed tank;  $T_2$ : storage tank; S: sampling point; P: peristaltic pump; V: valves. (b) R: reactor;  $S_{1-4}$ : oxygen, solid suspended, temperature and pH probes; D: settler; V: pneumatic pump (BAC)/peristaltic pump (AS);  $F_{1-3}$ : flowmeters; P: peristaltic pump; C: compressor; W: air flow;  $Q_i$ : wastewater flow;  $Q_p$ : purge flow;  $Q_c$ : treated water flow.

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