Journal of Cleaner Production 81 (2014) 120–129

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

New treatment of real electroplating wastewater containing heavy metal ions by adsorption onto olive stone

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ARTICLE INFO

Article history:
Received 10 March 2014
Received in revised form
27 May 2014
Accepted 11 June 2014
Available online 20 June 2014

Keywords:
Adsorption
Electroplating wastewater
Fixed-bed column
Heavy metals
Olive stone

ABSTRACT

The goal of this research was to develop new processes for the remediation of electroplating wastewater using olive stone as adsorbent material packed in fixed-bed columns. The study was performed with effluents containing chromium (VI), copper (II) and nickel (II) of an electroplating plant. First, we started our research from studying olive stone as an efficient biomaterial capable of removing chromium (VI) of both synthetic and real wastewater. The removal of chromium (VI) took place following two parallel mechanisms: the adsorption of chromium (VI) and the reduction of chromium (VI) to chromium (III) by contact with the biomass, appearing chromium (III) in the aqueous solution. Then, two fixed-bed columns were utilized for removal both chromium (VI) and chromium (III), in the first fixed-bed column, chromium (VI) was successfully removed and in the second column, the chromium (III). Finally, two types of adsorption experiments were selected for simultaneous adsorption of three metals: (1) with a first stage reduction of chromium and only one adsorption fixed-bed column; and (2) without the stage of reduction and two adsorption fixed-bed columns. The results showed that the second method was more suitable for the purposes of wastewater treatment. In the first column, chromium (VI) was completely removed. In the second column, the outlet concentration of heavy metals was 2.04, 1.48 and 0.93 mg/L for total chromium, copper (II), and nickel (II), respectively. This research provides a high efficient new alternative to clean industrial wastewater.

1. Introduction

Electroplating is the process of depositing the desired coating by means of electrolysis, i.e. applying electricity to an object to alter the characteristics of a surface in order to improve its appearance, protection, surface properties, engineering or mechanical properties or a combination of them. The process involves the dissolving of metal at the anode and depositing the metal at the cathode by passing electricity through the electrolytic bath. Some metals commonly used for electroplating are cadmium, chromium, copper, nickel, lead, zinc, or a combination of them. Electroplating and metal finishing techniques play an important role in the development of many metals manufacturing and other engineering industries in the world (Kanani, 2006).

Platters immerse objects into a series of chemical baths in order to change their surface conditions. The numbers of tanks and their chemical constituents differ depending on the desired result. The principal types of the electroplating wastewater are bath solutions and rinse waters. Every plating plant is different as well as their wastewater constituents (Bartkiewicz, 2006).

In general, wastewaters from electroplating operations contain relatively little organic matter but are highly toxic. Rinse waters are continuously produced and contain relatively low concentrations of contaminants. Bath solutions, in contrast, contain markedly higher concentrations of metals (on the order of hundreds of g/L) and are exchanged every several weeks or months, depending on the process (Bartkiewicz, 2006). High concentrations of toxic pollutants in electroplating effluents preclude the direct application of biological methods for their treatment. Thus, the removal of heavy metals from electroplating wastewater is a matter of paramount importance (Liu et al., 2013).

There are many physical, chemical, and biological methods currently being used for electroplating wastewater treatment: chemical precipitation, coagulation–flocculation, ion exchange, etc. Also, in recent years, some new methods are being studied, such as

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http://dx.doi.org/10.1016/j.jclepro.2014.06.036
0959-6526/

polishing in constructed wetlands (Sochacki et al., 2014), permeable reactive barriers (Liu et al., 2013), nanofiltration membrane technology (Wang et al., 2013), H_2O_2 oxidation followed by the anodic Fenton process (Zhao et al., 2013), combined electrochemical and ozonation methods (Orescanin et al., 2013), UV/TiO_2 photocatalysis (Hydaya et al., 2013).

Metal precipitation as hydroxides has been the most favored treatment option. However, precipitation, by adjusting pH values, is not selective process and produces large quantities of solid sludge for disposal (Eccles, 1995).

The goal of this research is to develop new processes for the remediation of electroplating wastewater containing three heavy metals (Cr (VI), Cu (II), and Ni (II)) using olive stone as adsorbent material packed in fixed-bed columns. This work has especially focused on Cr (VI) since it is the most toxic metal in the wastewater samples supplied by the company, which is found in higher concentrations thus posing more purification problems.

On the one hand, olive stone can be considered as a promising low-cost adsorbent, since this material is produced in great quantities in the Mediterranean area and, is of no market value (Blázquez et al., 2013). Spain is one of the Mediterranean countries which are in first range of olive and olive oil production. The annual production of olive oil in Spain is about 800,000 tons. The data reflect the importance of the olive oil sector in the Mediterranean area and consequently the magnitude of the problems related to the disposal of large amounts of wastes produced during olive oil production (Blázquez et al., 2011a).

On the other hand, key issues for the implementation of Integrated Pollution Prevention and Control Directive in electroplating processes are: "effective management systems, efficient raw material, energy and water usage, optimized use of chemicals in processes and directly related activities, the substitution by less harmful substances, minimization, recovery and recycling of waste, the prevention of environmental accidents and minimization of their consequences" and one indicative Best Available Technique is "consider use of ion exchange or other treatment unit to recirculate rinse waters".

For all that, the main specific objectives of the work were (1) investigating the different possibilities of remediation of electroplating wastewater utilizing olive stone under different experimental conditions; and (2) evaluating the removal efficiency of the co-existing heavy metals by olive stone in the different adsorption processes.

2. Materials and methods

This section provides sufficient detail about material and methods to allow the work to be reproduced.

2.1. Electroplating plant description

The study was performed with three effluents containing Cr (VI), Cu (II) and Ni (II) of an electroplating plant located in Toledo, Spain.

According to the information provided by the company, the wastewater samples containing Cu (II) and Ni (II) were obtained directly from the rinsing tanks (after plating has been done, the plated objects are rinsed with water). In turn, the samples containing Cr (VI) were collected from the plating tanks.

The existing treatment unit performs a chemical treatment to abate the heavy metal pollution caused by Cr (VI), Cu (II), and Ni (II). When an appreciable sludge accumulation occurs in the rinsing bath, the entire rinsing water is changed and the wastewater is drained out for treatment to the equalization tank.

Chrome, copper, and nickel streams were segregated due to the different characteristics of the streams. Firstly, the conversion of Cr (VI) into Cr (III) was enhanced by adding sodium meta-bi-sulphite to the chrome-containing wastewater according the following reactions (in case HSO_3^-, is in excess, the reduction of Cr (VI) follows Eq. (1); whereas the redox reaction follows Eq. (2) in the presence of excess of Cr (VI)) (Say Kee Ong, 2008)

$$2HCrO_4^- + 4HSO_3^- + 6H^+ \leftrightarrow 2Cr^{3+} + 3SO_4^{2-} + S_2O_6^{2-} + 6H_2O \quad (1)$$

or

$$2HCrO_4^- + 3HSO_3^- + 5H^+ \leftrightarrow 2Cr^{3+} + 3SO_4^{2-} + 5H_2O \quad (2)$$

This wastewater containing Cr (III) were combined with two other streams containing Cu (II) and Ni (II) to form a single stream. The final concentrations of metals in the effluent fed to the purification system fluctuated between 10 and 50 mg/L. Finally, the full wastewater pH was adjusted to the optimum value for the precipitation of the metals as hydroxides (7.5, 7.6 and 10.6 for Cr (III), Cu (II) and Ni (II), respectively). Heavy metals were precipitated via the typical hydroxide precipitation methodology according the following reactions (Chapman, 2004),

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3 \downarrow \quad (3)$$

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2 \downarrow \quad (4)$$

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \downarrow \quad (5)$$

In summary, the reduced trivalent chromium is precipitated in combination with other metal wastes by the addition of an alkali. This water will further be taken to flocculation to enhance the settling/separation of sludge from water. Finally, the pH of the final effluent is adjusted with sulphuric acid and discharged into a stream.

2.2. Characterization of wastewater

We analyzed the relevant parameters of the wastewater collected from the rinsing bath of copper and nickel plating units and from the plating tank of chrome. Table 1 shows the characteristics of the three wastewater samples provided by the company. The wastewaters are distinctively different in volume and characteristics. Solution of Cr (VI) from vats is highly concentrated while

Table 1
Main characteristics of the wastewater provided by the electroplating company.

Parameters		Cr wastewater	Cu wastewater	Ni wastewater
Origin		Plating tank	Rising tank	Rising tank
Temperature, °C		24	24	24
Color		Dark yellowish brown	Light blue	Light green
pH		0.50	7.65	7.01
Total suspended solids (TSS), mg/L		0	0	0
Heavy metal concentrations, mg/L	Chromium (VI)	42,000	0.000	0.000
	Copper (II)	2,980	1.100	0.000
	Nickel (II)	0.000	0.000	4,710
Conductivity, mS/cm		142.000	0.312	6.800
Total dissolved solid (TDS), g/L		90.400	0.200	4.380