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Remediation and recycling of chromium from tannery wastewater using combined chemical–biological treatment system

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ABSTRACT

Tannery wastewater containing chromium (Cr) is one of the most serious problems in leather industry. In order to develop an effective and eco-friendly treatment technology, a combined chemical–biological treatment system was performed for Cr remediation and recycling. The aim of the present study is to design a laboratory scale system using chemical precipitation of Cr(III) combined with biological removal of Cr(VI) from tannery wastewater, and to investigate the possibility of recycling the recovered Cr(III) in the tanning industry.

Chemical precipitation of Cr(III) was carried out using lime and cement dust. The actinomycete strain *Kitasatosporia* sp. was used in microcosm studies for Cr(VI) bioremoval. Moreover, parameters such as type of porous medium, inoculum size, flow rate and culture conditions were investigated. The precipitated Cr(III) that was recovered from the chemical precipitation stage was recycled in the leather tanning industry.

Our findings indicate that the maximum Cr(III) precipitation (98%) was achieved using 2 g/100 mL of lime and 2 h of settling rate. On the other hand, microcosm columns using sand that was inoculated with induced culture (OD_{600} = 2.43) and flow rate (2 mL/min) gave the maximum recovery (99%) of Cr(VI). The experimental Cr(III) was successfully recycled in the tanning process and the experimental leathers showed comparable properties as same as the leathers tanned with commercial Cr(III). Thus, we concluded that using combined chemical–biological treatment system for Cr remediation from tanning wastewater together with recycling process for the recovered Cr(III) is a promising strategy for economic and environmental friendly tanning industry.

1. Introduction

Chromium (Cr) is one of the major environmental pollutants coming from various industrial activities, such as leather tanning, electrolytic plating, metal finishing, petroleum refining and etc. (Acosta-Rodríguez et al., 2015). There are two stable forms of chromium in the environment, trivalent (Cr(III)) and hexavalent (Cr(VI)) chromium. However, Cr(VI) is more toxic than Cr(III) due to its high solubility and mobility in soil and aquatic environments, and high permeability through biological membranes (Marsh and McInerney, 2001; Shukla and Rai, 2006). Thus, it is considered as a risk pollutant by the United States Environmental Protection Agency (EPA: www.epa.gov).

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Tanning industry worldwide generates approximately 40 million L of wastewater containing Cr every year (Saranraj and Sujitha, 2013). In most of the countries, the tanning wastewater is discharged without proper treatment into the sewerage system causing serious environmental impact. Treatment of Cr polluted wastewater is mostly dependent on physico-chemical methods, such as chemical precipitation, reverse osmosis, membrane processes and adsorption (Ludvik, 2000; Kocaoba and Akin, 2002). However, chemical precipitation has been considered to be one of the most effective techniques to separate heavy metals from industrial wastewater (Barakat, 2011). Chemical precipitation is a process in which soluble metals and inorganics are converted to relatively insoluble forms (precipitates) by the addition of precipitating agents (Bennett et al., 1981). Substances used habitually to promote the precipitation are: calcium hydroxide, sodium hydroxide, magnesium oxide or calcium magnesium carbonate (Tsugita and Ellis, 1981; Hintermeyer et al., 2008). Subsequently the precipitated chromium hydroxide can be re-dissolved by acidification and be easily reused in the tanning process (Kanagaraj et al., 2008).

Supernatant from Cr precipitation process is relatively free of Cr(III). The biological treatment of such supernatant solution is one of the successful approaches to remove Cr(VI) (Lovely and Coates, 1997; Langerwerf, 1999; Rittmann et al., 2004). However, various fungal and bacterial species are reported for Cr(VI) bioremoval from industrial wastewater (e.g., Congeevarama et al., 2007; Das and Santra, 2012; Vermaa et al., 2015), there are a few studies concern the abilities of actinomycetes (More et al., 2001; Abdulla et al., 2010, 2011). The metabolic diversity and genomic characteristics of actinomycetes make them significant agents for bioremoval of metals from contaminated environments (Polti et al., 2007).

Combined chemical–biological treatment of Cr polluted wastewater became more economic and environmental friendly strategy than either physico-chemical or biological treatment alone (Abdulla et al., 2010, 2011). Such combined treatment leaves a lower concentration of Cr in the effluent than the other methods. Combined chemical–biological treatment of Cr has been approached from three directions (Ayres et al., 1994; Goswami and Mazumder, 2014): (a) biological treatment followed by chemical treatment as a polishing step, (b) chemical treatment at levels where the stoichiometry is effective and economic for treatment, followed by biological treatment as a polishing step, (c) chemical precipitation followed by biological treatment was also approached in a staged reactor system.

The present study aims to design a laboratory scale system using a combined chemical–biological treatment to remove Cr(III) and Cr(VI) from tannery wastewater, and to investigate the possibility of recycling the recovered Cr(III) in the tanning industry.

2. Materials and methods

2.1. *Sampling and characterization of tanning wastewater*

Wastewater samples were collected in clean 1000 mL polyethylene bottles from the outlet point of the chromium tanning stage of selected tanneries in Old Cairo, Egypt. The bottles were kept immediately in 4 °C until further analysis. The characteristics of the water samples, such as pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), sulfate, turbidity, salinity and electric conductivity (EC) were determined according to standard methods for the examination of water and wastewater (APHA, 1998). The other measurements were carried out as following:

a) Analytical estimation of Cr(VI) and Cr(III)

The concentration of Cr(VI) was determined spectrophotometrically using 1,5-diphenylcarbazide as complexing agent (Bartlett and James, 1996). Diphenylcarbazide stock solution (0.25% w/v in 50% acetone) was prepared. A volume of 15 mL of each sample was pipetted out into 25 mL standard flasks. Then 2 mL of H_2SO_4 (3 M) was added to the sample followed by 1 mL of diphenylcarbazide and the total volume was made up to 25 mL using distilled water. The solution was allowed to stand for 10 min, after which the absorbance of the purple-colored solution was measured using spectrophotometer (CECIL, CE 393, Series 2, UK) at 540 nm. Cr(VI) concentration was extrapolated from a standard curve prepared from standard solutions of potassium dichromate.

In order to estimate the concentration of total chromium, Cr(III) in samples was completely oxidized to Cr(VI) (Chandrachekhara et al., 2015; Onchoke and Sasu, 2016). Methyl orange was used as an indicator. A volume of 15 mL of each sample was pipetted out into 25 mL standard flasks. Then 1 mL of H_2SO_4 was added and the total volume was made up to 40 mL using distilled water. The mixture was heated till boiling. Then 2 drops of $KMnO_4$ were added to give a dark red color followed by 1 mL of NaN_3 and continue boiling gently for 30 s. The total chromium concentration was estimated using the same colorimetric method as for Cr(VI) estimation.

The concentration of Cr(III) was obtained by calculating the difference between the values of total Cr concentration and Cr(VI) concentration as estimated by the above procedures (Bartlett, 1991).

b) Enumeration of microbial cells in tanning wastewater

One milliliter of wastewater samples were serially diluted in phosphate buffer and 0.1 mL of the suitable dilutions were plated onto duplicates of the appropriate media using spread plate technique. Dilutions up to 10^{-3} and 10^{-4} were used for enumeration of actinomycetes on starch casein agar amended with cyclohexamide (0.05 g/L) to inhibit fungal growth. Plates were incubated at 28 °C for 10–14 days. Bacteria were enumerated using nutrient agar; plating was performed from dilutions 10^{-3} and 10^{-4} and was incubated at 37 °C for 24–36 h. Fungi were enumerated using Czapek–Dox agar; plating was performed from dilutions 10^{-3} and 10^{-4} and plates were incubated at 28 °C for 4 days.

2.2. *Set-up of combined chemical–biological treatment system for tannery wastewater*

The treatment system was designed in two stages, (a) chemical precipitation of Cr(III) from raw tannery wastewater, and (b) biological removal of Cr(VI) from pre-treated tanning wastewater (the supernatant of the precipitation stage).

2.2.1. *Chemical precipitation of Cr(III)*

The chemical precipitation was performed according to Abdulla et al. (2010). Thirteen glass jars were filled with 100 mL tannery wastewater. Lime and cement dust were added with different concentrations from 0.5 g to 3 g per 100 mL. The stirring was continued for 10 min with rapid mixing of 100 rpm by orbital shaking, followed by slow mixing for 5 min at 40 rpm. The jars were allowed to settle then samples were taken from the supernatant for Cr(III) analysis (according to the above method) at intervals of 30 min for 3 h.