Chemosphere 264 (2021) 128487

Contents lists available at ScienceDirect

Chemosphere

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

New insights in the slow ligand exchange reaction between Cr(III)-EDTA and Fe(III), and direct analysis of free and complexed EDTA in tannery wastewaters by liquid chromatography - Tandem mass spectrometry

Marco Roverso [a], Valerio Di Marco [a], Gabriella Favaro [a], Iole Maria Di Gangi [a], Denis Badocco [a], Mirco Zerlottin [b], Daniele Refosco [b], Andrea Tapparo [a], Sara Bogialli [a, *], Paolo Pastore [a]

[a] Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131, Padova, Italy
[b] Acque Del Chiampo S.p.a, Servizio Idrico Integrato, Via Ferraretta, 20, 36071, Arzignano (Vi), Italy

HIGHLIGHTS

- Cr(III)-EDTA identified for the first time with a direct measurement in wastewaters.
- New HPLC-MS procedure to determine free and complexed EDTA in wastewaters.
- Elimination of a systematic bias in the determination of EDTA.
- Rationalization of the reaction kinetics of a Cr-EDTA dissociation in water.

ARTICLE INFO

Article history:
Received 14 April 2020
Received in revised form
17 September 2020
Accepted 28 September 2020
Available online 1 October 2020

Handling Editor: Petra Petra Krystek

Keywords:
EDTA complexes
Chromium complexes kinetics
Wastewaters
Liquid chromatography-mass spectrometry

ABSTRACT

EDTA and soluble Cr(III) are usually both present in wastewaters coming from treatment plants handling tannery effluents. A well-established method to determine EDTA is based on the conversion of free and complexed EDTA into its Fe(III) complex. This procedure gives inconsistent data when Cr(III)-EDTA is present. This fact was here demonstrated by studying the kinetics of the exchange reaction between Fe(III) and Cr(III)-EDTA at 90 °C and various pH values, from acidic to neutral. The reaction is very slow (several weeks); the slow kinetics of conversion of Cr(III)-EDTA to Fe(III)-EDTA is even more accentuated at room temperature and the low concentrations of reactants in wastewaters. The presence of EDTA complexes of Fe(III) and Cr(III) was demonstrated in industrial effluents and wastewaters by developing a selective method based on liquid chromatography-tandem mass spectrometry (LC-MS/MS), which was able to detect free and complexed EDTA at concentration levels <1 μM. A systematic underestimation of the EDTA expressed as Fe(III) complex was demonstrated in samples containing Cr(III)-EDTA. Cr(III)-EDTA was identified for the first time as a component of wastewater samples at a concentration level of about 2 μM and turned out to be an inert species that significantly contributes to the final soluble Cr amount. This study gives new insights into the inertness of Cr(III) toward metal exchange equilibria of EDTA complexes, resolves a bias in the analysis of total EDTA in samples containing Cr(III)-EDTA, allowing the direct determination of free and complexed EDTA by LC-MS.

1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is extensively used as sodium salts in leather processing mainly to prevent iron stains. Technical documents for the tanning industry recommend the replacement of EDTA because it is poorly biodegradable (Kaluza

* Corresponding author.
E-mail address: sara.bogialli@unipd.it (S. Bogialli).

https://doi.org/10.1016/j.chemosphere.2020.128487
0045-6535/