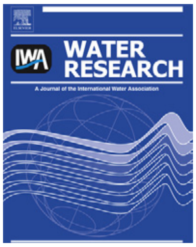
WATER RESEARCH 45 (2011) 3933–3940

Available at www.sciencedirect.com

ScienceDirect

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



Characterisation of the impact of coagulation and anaerobic bio-treatment on the removal of chromophores from molasses wastewater

Linhua Fan[*], *Thang Nguyen*, *Felicity A. Roddick*

School of Civil, Environmental and Chemical Engineering, RMIT University, 124 La Trobe Street, Melbourne, Victoria 3001, Australia

ARTICLE INFO

Article history:
Received 27 October 2010
Received in revised form
28 April 2011
Accepted 30 April 2011
Available online 10 May 2011

Keywords:
Coagulation
Decolourisation
Melanoidins
Characterisation
Molasses wastewater

ABSTRACT

The performance of a coagulation sequence using aluminium chlorohydrate (ACH) and a low MW polydiallyldimethylammonium chloride (polyDADMAC), and ferric chloride, for decolourising a high-strength industrial molasses wastewater was compared at bench scale. At their optimum dosages, ACH/polyDADMAC gave higher colour removal than $FeCl_3$ (45% cf. 28%), whereas COD reduction was similar (~30%), indicating preferential removal of melanoidins (a major contributor to the colour) by ACH/polyDADMAC. Size exclusion chromatography and fluorescence excitation–emission matrix spectrometry suggested that chromophoric Fe–organic complexes were formed during $FeCl_3$ treatment of the molasses wastewater, which appeared to compromise decolourisation efficiency. Anaerobic bio-treatment of the wastewater enhanced the coagulation efficiency markedly, with $FeCl_3$ achieving 94% colour and 96% COD removal, while ACH/polyDADMAC gave 70% and 56% removal, respectively. The improved decolourisation was attributed to the decrease in low MW organics (<500 Da) and biopolymers by the biological treatment, leading to reduced competition with melanoidins for interaction with coagulant/flocculant. For both the wastewater and the biologically treated wastewater, ACH/polyDADMAC treatment gave flocs with markedly better settling properties compared with $FeCl_3$.

1. Introduction

Molasses, a sugar-rich by-product from sugar production processes, is commonly used as a raw material in the fermentation industries. Molasses wastewater from industrial fermentation processes is typically high in colour and organic load, consequently this limits its direct discharge to the aquatic environment, and even to wastewater treatment plants. The origin of the colour in the molasses wastewater is primarily associated with the dark brown melanoidin pigments which are the products of the non-enzymatic reaction between sugars and amino acids, peptides or proteins (Maillard Reaction) (Kort, 1979). Melanoidins are generally regarded to be heterogeneous, high molecular weight (MW), negatively charged, acidic and highly dispersed polymers with similar chemical properties to humic substances (i.e., humic and fulvic acids) (Migo et al., 1993). However, the detailed structure and characteristics of the melanoidins are not yet fully understood, thus hindering the development of effective processes for their removal (Satyawali and Balkrishnan, 2008).

Many methods have been investigated for reducing colour and COD of melanoidin-containing wastewaters, including activated carbon adsorption (Mall and Kumar, 1997); coagulation and flocculation (Migo et al., 1993); oxidation using ozone

---

[*] *Corresponding author*. Tel.: +61 3 9925 3692; fax: +61 3 9925 3746.
E-mail address: linhua.fan@rmit.edu.au (L. Fan).

0043-1354/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2011.04.050

(Kim et al., 1985; Peña et al., 2003), UV/H_2O_2 or UV/H_2O_2/Fe (II) (Catalkaya and Sengül, 2006; Dwyer et al., 2008); bioremediation using white-rot fungi (Kahraman and Yesilada, 2003) or acetogenic bacteria (Sirianuntapiboon et al., 2003), electro-oxidation (Cañizares et al., 2009) and membrane filtration (Mutlu et al., 2002). Of these, coagulation/flocculation is regarded as a simple and cost-effective means of decolourising molasses wastewater (Zhou et al., 2008; Liang et al., 2009a).

A range of conventional inorganic coagulants has been tested for removing colour and organics from melanoidin-containing wastewaters. Ferric chloride was reported to perform better than other coagulants including alum, aluminium chloride, ferric sulphate and polyferric sulphate (PFS) in the treatment of a biologically treated molasses wastewater, with up to 89% and 98% reduction for COD and colour, respectively (Liang et al., 2009a,b). However, poorer settleability of the flocs for the ferric chloride-treated wastewater was observed, and this combined with the corrosive/highly acidic nature of the ferric chloride remained a critical issue limiting its industrial application. Polyelectrolytes are used in water and wastewater treatment both for coagulation and as coagulant/flocculant aids to strengthen flocs and improve their settleability through charge patching and particle bridging. Cationic polyacrylamide was reported to markedly enhance floc settleability of a molasses wastewater after primary coagulation using ferric chloride, whereas anionic polyacrylamide had little effect (Liang et al., 2009a). However, polyacrylamides did little to improve colour and organic removal from the wastewater. Nevertheless, the use of other polyelectrolyte types, such as high charge density cationic polyDADMACs for molasses wastewater treatment has not been documented.

The aims of this study were to investigate the effectiveness of sequential ACH/polyDADMAC treatment of a highly coloured molasses process wastewater, and to evaluate the treatability of the wastewater by coagulation before and after anaerobic biological pre-treatment. Coagulation tests with ferric chloride were conducted in parallel for comparison. Size exclusion chromatography (SEC) analyses using liquid chromatography with organic carbon detection (LC–OCD) and UV absorbance detection (LC–UVD), and fluorescence excitation–emission matrix (EEM) spectrometry, were employed in order to gain a better insight into the impact of the coagulation and bio-treatment on the removal of chromophores from the molasses wastewaters.

2. Materials and methods

2.1. Wastewater samples

Wastewater samples containing molasses (of cane origin) were collected from an industrial fermentation plant in Victoria. Two types of wastewaters were generated from the production process: the first pass (i.e., the very high-strength process supernatant) and second pass wastewater (i.e., product washings). The wastewater tested in this study was the mixture of the two wastewaters at a ratio of 40% first pass to 60% second pass, which was the typical composition of the wastewater discharged to sewer as Trade Waste. Part of the molasses wastewater sample was subjected to anaerobic treatment using a lab-scale unit in a commercial laboratory, and the treated effluent was supplied for the coagulation tests. The characteristics of the wastewater (WW) and the anaerobically treated wastewater (ATW) are summarised in Table 1.

Table 1 – Characteristics of WW and ATW.

Parameter	WW	ATW
pH	5.6–6.0	7.7–8.5
True colour (mg Pt–Co L^{-1})	30,000–35,500	31,000–36,000
DOC (mg L^{-1})	8200–12,000	3200–3900
COD (mg L^{-1})	18,000–30,000	6000–14,000
UVA_{254} (cm^{-1}, 1/1000 dilution)	0.1–0.15	0.13–0.16

Note: Data are given in ranges based on the measurements of 5 samples collected over a period of 6 months.

2.2. Coagulants/flocculants and test procedures

ACH (aluminium chlorohydrate), sold as Megapac 23 (40% w/w), was supplied by Omega Chemicals. Ferric chloride ($FeCl_3$) was supplied by BDH Pty Ltd. PolyDADMACs were supplied as Magnafloc LT410 (MW ~100 kDa), LT510 (MW 200–350 kDa), LT610 (MW 400–500 kDa), and Zetag 7120 (MW ~1000 kDa) by Ciba Specialty Chemicals P/L.

Coagulation trials were conducted using 2 L wastewater for each run with a laboratory jar tester (Phipps and Bird, PB-700) at the solution temperature of 22 °C with rapid mixing for 2 min at 250 rpm followed by slow mixing for 20 min at 30 rpm. The coagulated water was settled for 2 h and the supernatant was then analysed. For sequential ACH/polyDADMAC treatment, ACH was added to the wastewater and mixed at 250 rpm for 2 min. PolyDADMAC was then added to the solution and mixed at 250 rpm for a further minute, followed by slow mixing at 30 rpm for 20 min. Doses were as noted in the text. ACH dosages are reported in terms of pure ACH. All coagulation tests and bulk analyses were conducted in duplicate on two wastewater samples collected on different dates. The overall trends in colour and COD reduction for the two wastewater samples were in good agreement. As the variation of the measured colour and COD values was generally less than 5% for each wastewater sample, only one set of colour and COD reduction data and the associated SEC and fluorescence EEMs data were presented.

The settling properties of the wastewater and anaerobically treated wastewater treated with $FeCl_3$ or ACH/LT410 were characterised by measuring the residual turbidity and floc settling rate. The settling rate was determined by transferring the coagulated wastewater sample to a 1 L measuring cylinder, and the volume of the sludge layer (floc) was recorded at 30, 90, 150 and 210 min. The sludge production for the coagulation treatments was estimated using a sludge mass balance (SMB) model. The SMB model is based on the possible sources of suspended solids contributing to the total sludge produced during the wastewater coagulation processes (Cornwell, 1999), and can be expressed by

$$\text{Sludge production}\ (\text{kg ML}^{-1}) = \text{TSS} + \text{X} + \text{Fe} + \text{Mn} + \text{Al} + \text{D} + \text{C}$$