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Effect of electron donor source on the treatment of Cr(VI)-containing textile wastewater using sulfate-reducing fluidized bed reactors (FBRs)

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HIGHLIGHTS

- SRB has the ability to reduce Cr(VI) to Cr(III) and azo dye reduction simultaneously.
- The removal rate of azo dye is dependent on the type of electron donor source.
- FBRs perform well in terms of COD, sulfate, color and Cr(VI) removals.

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ABSTRACT

The treatment of Cr(VI) containing textile wastewater was studied in ethanol and glucose-fed sulfate-reducing fluidized bed reactors at 35 °C for around 250 days. The synthetic wastewater contained Cr(VI) (5–45 mg L^{-1}), azo dye (Remazol Brilliant Violet 5R) (100–200 mg L^{-1}), sulfate (2000 mg L^{-1}) and ethanol or glucose (2000 mg L^{-1} chemical oxygen demand (COD)). The robustness of two FBRs was assessed under varying Cr(VI) and azo dye loadings. Both reactors performed well in terms of COD, sulfate, color and Cr(VI) removals. However, ethanol-fed FBR performed better than glucose-fed one. The COD, sulfate, chromium and color removals at the highest Cr(VI) concentration (45 mg L^{-1}) in ethanol-fed FBR were around 75%, 95%, 93%, and 99%, respectively. Further increase in influent Cr(VI) concentration adversely effected reactor performance. The COD, sulfate, chromium and color removals at 45 mg L^{-1} Cr(VI) in glucose-fed FBR were around 60%, 50%, 93%, and 76%, respectively.

1. Introduction

The textile industry wastewaters are known as one of the main sources of severe pollution problems worldwide. In particular, the release of highly colored effluents is undesirable, due to toxic and resistant characteristics (Weisburger, 2002). In addition to color, typical textile wastewater industry is characterized by high chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, and salinity (Dos Santos et al., 2007). The color mainly comes from dying process in which many chemicals such as heavy metal containing dyes (chromium, cadmium, zinc etc.), nitrate and sulfate containing salts, surfactants, sulfide and formaldehyde, may be added to improve dye fixation. It has been reported that sulfate is generally added to the dye baths for ionic strength adjustment or it may be formed by the oxidation of sulfur species used in dyeing processes, such as sulfide, hydrosulfide, and dithionite (van der Zee et al., 2003). Additionally, the most frequently detected heavy metal in textile industry wastewaters is chromium. It has been reported that in wool dyeing process, its concentrations can reach as high as 50 mgCr L^{-1} (Bisschops and Spanjers, 2003).

The chromium has an oxidation stage between (−II) and (+VI) among which trivalent (Cr(III)) and hexavalent (Cr(VI)) are the most common chromium species in the environment (Vaiopoulou and Gikas, 2012). Although Cr(III) is required in trace amounts for living organisms, Cr(VI) is well-known carcinogen and to be removed from wastewater before discharge. Microbial Cr(VI) reduction is one of the approaches used for the detoxification of Cr(VI)-containing wastewater. Cr(VI) can be reduced in biological treatment processes to Cr(III), almost insoluble and less-toxic chromium form (Agrawal et al., 2006).

Biological methods are commonly considered to be the most effective treatment applications since they present lower operational costs and environmentally safe. Recent studies indicated success of FBRs in biological treatment of various types of wastewaters (Sen and Demirer, 2003; Sahinkaya et al., 2011). Anaerobic

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treatment is essential to remove color from textile wastewater. Under anaerobic conditions, color is removed by oxidation–reduction reactions in which azo dye and organic compounds in wastewater act as electron acceptor and electron donor, respectively. The importance of sulfate reducing bacteria (SRB) on azo dye reduction has been reported in previous studies (Cervantes et al., 2006, 2007; van der Zee et al., 2003). Additionally, it has been reported that certain heavy metals such as Cr(VI) may be reduced under sulfate-reducing conditions (Chang et al., 2000; Sahinkaya et al., 2012a,b). The literature studies mentioned above have shown the possibility of simultaneous removal of COD, color and Cr(VI) from textile industry wastewaters.

Organic compounds often act as electron donor in microbial Cr(VI) reduction processes. The type and the concentration of organic substrate affect the rate of microbial respiration in the presence of Cr(VI) (Cokgor et al., 2007). In this context, this study aims at evaluating the efficiency of ethanol- and glucose-fed sulfate-reducing fluidized bed reactors treating sulfate-, Cr(VI)- and color-containing simulated textile wastewater.

2. Methods

2.1. Simulated textile wastewater

The synthetic textile effluent (Table 1) fed to the reactors was composed of sulfate, azo dye Cr(VI) and nutrients required for microbiological growth. All inorganic nutrients were provided in excess not to limit biological activity. Sulfate in synthetic wastewater was kept constant at 2000 mg SO_4^{-2} L^{-1} throughout the study. The studied azo dye was the monoazo reactive dye Remazol Brilliant Violet 5R (C.I Reactive Violet 5), (Sigma–Aldrich, Germany). Azo dye concentration in the synthetic wastewater was 100 or 200 mg L^{-1} to study the treatment of highly colored textile wastewater. Ethanol and glucose (contributed to COD of 2000 mg L^{-1}) were used to provide readily biodegradable carbon source for the ethanol- and glucose-fed sulfate-reducing fluidized bed reactors, respectively. Potassium dichromate ($K_2Cr_2O_7$) was added to synthetic wastewater to have predetermined concentrations (Table 1).

2.2. Bioreactors setup and operation

Two laboratory scale glass fluidized bed reactors (FBRs) were used to treat simulated textile wastewater. The FBRs were inoculated with anaerobic digester effluent to have an initial volatile suspended solids content of 3 g L^{-1} in the reactors. After supplementation of sludge, the reactors were run in recirculation mode for 2 days without feeding to let the biomass to attach on the carrier material. The FBRs were operated in a temperature controlled room at 35 °C. Granular activated carbon (1–1.5 mm) was used as carrier material for the both reactors. Reactor 1 had an empty bed volume of 450 mL and fed with ethanol as carbon and electron source. Reactor 2 had an empty bed volume of 750 mL and fed with glucose as carbon and electron source. The effluent of the reactors was recycled to achieve around 10–15% fluidization of the column bed. The reactors were operated under varying dye and Cr(VI) concentrations (Table 2). Before experiments were started (start-up period), SRB were enriched in both reactors for around 2 months. In the first period (period I, days 0–62), both reactors were fed with 100 mg L^{-1} azo dye containing wastewater. Azo dye concentration was increased to 200 mg L^{-1} in period 2 (days 62–153). Then, azo dye concentration in the feed was kept constant at 200 mg L^{-1} and Cr(VI) reduction ability of the FBRs was assessed by gradually increasing the Cr(VI) concentration in the synthetic feed (Table 2). HRT in reactor 1 was kept constant at 14 h throughout the reactor operation. In the reactor 2, HRT was 24 h until period IV and decreased to 16 h in the last period (Table 2). Due to lower sulfate reduction rate of glucose-fed FBR compared to the ethanol-fed one, the HRT in glucose-fed bioreactor was kept longer. Operational conditions of FBRs were changed after steady state operational conditions were obtained, which was decided when the measured effluent parameters did not fluctuate appreciably (less than 10%). The effluents of the both reactors were sampled three times a week for the measurement of pH, alkalinity, COD, sulfate, Cr(VI), azo dye and dissolved sulfide. The feed of the reactors were sampled once a week and the same parameters (except sulfide) were measured.

Table 1
Composition of synthetic wastewater.

Component	Concentration (mg L^{-1})	
	Ethanol-fed FBR	Glucose-fed FBR
Ethanol	2000 as COD	–
Glucose	–	2000 as COD
$MgSO_4{\cdot}7H_2O$	2562.5	2562.5
Na_2SO_4	1480	1480
KH_2PO_4	56	56
NH_4Cl	110	110
Ascorbic acid	11	11
Sodium thioglycollate	14	14
Cr(VI)	5–45 (Table 2)	5–45 (Table 2)
Remazol Brilliant	100–200 (Table 2)	100–200 (Table 2)

Table 2
Operational conditions of FBRs. Sulfate and COD feed concentrations were kept constant at 2000 mg L^{-1} throughout the study.

	Days	HRT (h)	Azo dye (mg L^{-1})	Cr(VI) (mg L^{-1})
Periods for reactor 1 (ethanol-fed)				
I[a]	0–62	14	100	–
II	62–153	14	200	–
III	153–172	14	200	5
IV	172–194	14	200	20
V	194–222	14	200	45
Periods for reactor 2 (glucose-fed)				
I	0–62	24	100	-
II	62–153	24	200	-
III	153–172	24	200	5
IV	172–194	24	200	20
V	194–222	16	200	45

[a] Initial COD concentration was 1500 mg L^{-1}, then increased and kept constant at 2000 mg L^{-1} after day 33.

2.3. Batch adsorption tests

Two different sets of adsorption studies were conducted. In one set, the adsorption of dye on carrier material was studied. In another set of experiments, Cr(VI) adsorption on carrier material was studied. Adsorption tests were conducted in 500 mL glass bottles containing 300 mL solution. The batch reactors for the dye adsorption tests included 100 mg L^{-1} azo dye and 0.3, 0.6, and 1 g L^{-1} granule activated carbon used as carrier materials in FBRs. In the Cr(VI) adsorption studies, activated carbon concentration was kept at 5 g L^{-1} and Cr(VI) concentrations were adjusted as 50, 100, 200, 250 or 500 mg L^{-1}. Batch tests were performed in a shaking incubator at 35 °C. Samples were drawn at different time intervals for color and Cr(VI) measurements.

2.4. Analytical procedures

Before the measurements of sulfate, dissolved sulfide, Cr(VI), color (azo dye) and COD, liquid samples were centrifuged using a Hettich Rotofix 32 centrifuge at 3000*g* for 10 min. Azo dye