Removal of colour and organic matter from textile wastewaters using two anaerobic processes

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Received 25 February 2019; Accepted 28 July 2019

ABSTRACT

In this study, textile wastewater containing dye was treated using two anaerobic processes and then the dye degradation was studied. Textile wastewater was treated using a two-stage anaerobic system that included an anaerobic fermenter and a methane reactor. After a hydraulic retention time (HRT) of 3 d in the fermentation reactor, the maximum colour removal was 86% in the wastewater with the most colour (355 as Pt-Co). After the methane reactor, this value was 74%. When the removal of organic matter at different HRTs was examined, it was noted that 20%–30% of the removal occurs in the fermentation reactor. This is because the organic matter in the fermentation reactor was transformed by anaerobic bacteria into different organics (volatile fatty acids, alcohol, amines, etc.). However, as the HRT in the methane reactor increased, the removal of organic matter is increase to 95%. When the HRT in the methane reactor was 3 d, the chemical oxygen demand removal efficiency was around 84%. Therefore, 3 d was accepted as the optimum HRT in the anaerobic hybrid up-flow anaerobic sludge bed and was also found to be the optimum HRT in the fermentation reactor.

Keywords: Textile industry; Wastewater; Two-stage anaerobic process; Fermenter; Hybrid UASB

1. Introduction

The textile industry, which has recently experienced rapid growth, has been attracting attention recently for its environmental impact and current production dimensions. According to data from the textile and ready-wear sectors, global exports total \$766.15 billion, of which Turkey exports \$27.6 billion [1]. The textile sector is the most polluting among all industries [2] and it has a very serious impact on the environment. For example, 0.08–0.15 m³ of water are used per kilogram of fabric produced [3], and 1,000–3,000 m³ of water are used for every 12–20 tons of fabric processed per day [4,5]. Water used in dyeing and finishing must be treated to remove pollutants before it is discharged. The industry produces large quantities of this liquid waste, and the production process makes the composition of the wastewater

variable and toxic [6]. Untreated or partially treated discharged wastewater affects the life of phototrophic organisms by reducing the penetration of sunlight into water. In addition, suspended solids and oils dissipate in the air-water interface, and this significantly inhibits the oxygenation of water bodies. It is therefore necessary to remove this pollution with an appropriate treatment process before wastewater is discharged. Physico-chemical treatment processes, such as Fenton oxidation and ozonation, are frequently used in the treatment of wastewater from this industry. However, these systems also have significant disadvantages, such as excessive sludge production and dangerous the final products. In a study examining reactive and acid dyes, the Fenton oxidation process was reported to produce aromatic amines and excessive sludge [7]. On the other hand, ozonation and electrochemical advanced oxidation processes are known to oxidize chloride to form chlorinated by-products [8-10],

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Presented at the 4th International Conference on Recycling and Reuse 2018 (*R&R2018*), 24–26 October 2018, Istanbul, Turkey. 1944-3994/1944-3986 © 2019 Desalination Publications. All rights reserved.

and the use of this process in biological treatment systems is quite common [7,11,12]. An additional concern is that these two systems have high operating costs, and biological treatment systems with lower operating costs are preferred. In the literature, many aerobic-anaerobic biological treatment processes have been reported to have high removal efficiencies when treating synthetic textile wastewater [13-15]. However, in some studies conducted with real wastewater, significant toxicity in the water treated by the anaerobic reactor has been reported [16,17]. The two-stage anaerobic system, however, has proven very effective at treating wastewaters, including those with high salinity and toxicity, such as the textile industry. Therefore, in this study the effectiveness of colour and toxicity removal from effluent using a two-stage anaerobic process was investigated, and the operating parameters of this process were optimised.

2. Materials and methods

2.1. Reactors

Reactors, which were made of glass, were used in the two anaerobic processes. The first was a completely stirred fermentation reactor (3 L), and the second was a hybrid up-flow anaerobic sludge bed (UASB) (13 L) (Fig. 1). Used together, these two reactors are called a two-stage anaerobic treatment process and have been used effectively on many wastes and wastewater.

2.2. Analysis

Textile wastewater samples were taken from three textile factories located in Turkey's Denizli and Istanbul Industrial zones. The chemical and physical characterisations of real and synthetic wastewater samples are given in Table 1. Chemical oxygen demand (COD), total organic carbon (TOC), five-day biological oxygen demand (BOD₅), alkalinity, total suspended solids, mixed liquor volatile suspended solids (MLVSS) and volatile suspended solids were analysed according to the Standard Methods [18]. A Hach DR5000 UV-Vis spectrophotometer (Loveland, Colorado, USA) was used for colour and absorbance measurements. Conductivity and pH measurements were done using a Hach HQ40D portable multimeter (Loveland, Colorado, USA). TOC measurements were carried out with a Shimadzu TOC-CPN TOC analyser (Kyoto, Japan). A Hewlett Packard 6890 FID (Palo Alto, California, USA) was used to identify the specific volatile fatty acids (VFAs) produced during dark fermentation and their concentrations.

Table 1 Textile industry wastewater characteristics

Parameters	Range
BOD ₅ , mg BOD ₅ /L	128–130
COD _T mg COD/L	487–539
TOC, mg TOC/L	325-430
pH	7.32-8.56
Conductivity, mS/cm	8.48-14.52
Total solids, %	0.41-0.61
Chloride, mg Cl/L	1,700-4,049
Colour, Pt-Co	292–528
TKN, mg TKN/L	38-74
Orthophosphate, mg PO ₄ ³⁻ /L	0.42-1.21
Pt-Co	130–355



Fig. 1. Two-stage anaerobic biological wastewater treatment system.

The produced gas composition in terms of $H_{2'}$ CO₂ and CH₄ was analysed using a Varian 490-Gas chromatography (Palo Alto, California, USA).

2.3. Biological treatment

After the organic matter and colour in the wastewater were degraded in the fermentation reactor, the COD was removed by the UASB. At this point, the pollutants in the wastewater could be converted by the fermentation reactor into valuable media products such as hydrogen, methane, carbon monoxide and VFAs and fatty alcohols, which are the precursor components for biofuels. The pH in the fermentation reactor was controlled at 6-6.5 hydraulic retention time (HRT), which indicates that the retention time of the wastewater in the reactors was changed from 8 h to 7 d in both. The sludge retention time (SRT) of the fermenter reactor was determined to be 10-20 d or more, and at the methane reactor, to be infinite. The Food/Microorganism (F/M) ratio is expressed as the ratio of biomass in the reactor to the substrate and is commonly used for the design and control of the biological process in wastewater treatment plants. The F/M ratio in the fermenter reactor was selected in the high range of 3-4 g BOD_s/MLVSS. In many previous studies, the F/M ratio has been in the range of 1-10 [19,20]. To keep improving treatment efficiency, the F/M in the methane reactor was the same as in conventional anaerobic reactors, which have a ratio of about 0.3-0.4. Substances that have toxic effects on bacteria are produced by the degradation of textile wastewater, including salt and dyestuffs, in the anaerobic environment. The acute toxicity of the raw and treated wastewater was evaluated using Microtox toxicity tests. A bacterial (Vibrio fischeri) luminescence inhibition test called Lumistox, developed by Dr. Bruno Lange from Düsseldorf, Germany, was conducted according to ISO guidelines [21]. Granular sludge was used as the inoculum in this study, and it was collected from a full-scale UASB digester in an Istanbul brewery. To enrichment of acidification bacteria in seed sludge used in the fermentation reactor was used in the thermal treatments. The seed sludge was boiled for approx. 1 h at approx. 80°C, and then it was incubated under conditions suitable for germination. Many studies have reported that the thermal operations needed for acidification bacteria: short-time boiling (80°C-110°C), sterilisation (~121°C) and freezing/thawing (-20°C/25°C) [22,23]. The incubation period was realised as follows: CaCO₃ (3%) was added to each bottle to stabilize pH, and then samples were cultured for 12 h with constant agitation at 200 rpm and at a temperature of 30°C in an anaerobic media [24].

3. Results

3.1. Colour removal

Before entering into the UASB reactor, the efficiency of the colour removal from the wastewater by the fermentation reactor was very high, but the wastewater still contained a large amount of organics. With an HRT of 2 d, the colour removal from the effluent in the fermentation reactor was determined to be low at both SRTs (10–20 d), but this situation was same in the methane reactor also (Fig. 2). In this experimental process, a bacterium-free reactor (called a blank) was fed with the same raw wastewater, and at the end of the treatment, no change in the colour of the wastewater was observed. When the SRT in the fermentation reactor was 10 d, a very high colour removal (with an HRT of 3 to 7 d) was obtained (Figs. 3 and 4). In addition, the efficiency of dye removal in the methane reactor was determined as lower than that of other HRTs.

Studies have also been carried out using the Pt-Co method to determine the colour removal efficiency of each of the reactors. However, an SRT of 10 d gave the highest values in terms of colour removal in all HRTs, while in the methane reactor, colour removal remained low. When colour removal in the methane reactor was examined, there was no increase in colour removal efficiency with an increase in HRT. In the fermentation reactor, the minimum Pt-Co value



Fig. 2. UV-vis spectrum of fermentation and methane reactor effluents in HRT 2.



Fig. 3. UV-vis spectrum of fermentation and methane reactor effluents in HRT 3.

is lowest when the SRT is 10 d and the HRT is 3 d. At the end of treating this wastewater, which was original coloured blue, purple and green, it was observed that the colour had vanished (Fig. 5). The best results achieved in this study were with an HRT of 3 d in the fermenter reactor, after which the average colour removal was 61% (Pt-Co) and the maximum was 86%. In the methane reactor, these values were 35% and 74%, respectively (Fig. 6).

3.2. COD Removal

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When the COD removal was examined for different HRTs, the COD removal was between 15%–28% (Fig. 7). This COD removal efficiency is acceptable for anaerobic fermentation reactors. For example, at an HRT of 2 d (SRT at 10 and 20 d), gases occurred, and these were mainly hydrogen, carbon dioxide, methane and carbon monoxide. In the fermentation, hydrogen, which is regarded as a valuable medium product, was dominant at the beginning of the study in both

Raw 3,5 Ferm 20 Ferm 10 3,0 Methane 2,5 Absorbance 2,0 1,5 1,0 0.5 0,0 300 400 500 600 700 Wavelength (nm)

Fig. 4. UV-vis spectrum of fermentation and methane reactor effluents in HRT 7.

SRTs. However, entering of the wastewater to fermenter reactor continuously, it changed the microorganisms composition and stopping the production of hydrogen (Fig. 8). Gas compositions that formed in the hybrid reactor in different HRTs can be seen in Fig. 9.

However, as the HRT in the methane reactor increased (e.g., at 7 d), the COD removal was exceeded to 95%. This high HRT causes a significant increase in the reactor volume and, therefore, an increase in the need for space and the operational costs. Because of this, 3 d of HRT was accepted as an ideal operational parameter. When the HRT was 3 d, the COD removal efficiency was around 84%, establishing that the HRT was sufficient for treatment in the anaerobic regime of that kind of wastewater. Textile wastewater is often characterised by a low BOD/COD ratio, which can have an adverse effect on biological treatment [25–27]. The BOD/COD values were 0.06–0.358. A BOD/COD ratio of less than 0.4 indicates low biodegradability and requires a longer retention time in the biological treatment process to prevent a lower organic removal efficiency.



Fig. 6. Effluent colour change from various HRTs using the Pt-Co scale.



Fig. 5. (a) Raw wastewater, (b) Fermentation reactor's effluent and (c) Single hybrid UASB reactor and two-phase 2P (Fermentor – hybrid UASB) effluent.

3.3. Toxicity

The textile industry uses a large amount of water in its processes, and this water contains a significant amount of hazardous paints, salts, surfactants, chemicals and many additives [28,29]. The presence of very small amounts of dye can have a serious effect on the aesthetic quality, transparency and dissolved oxygen concentration in the water of lakes and rivers [30–32]. In the fermentation reactor, toxicity was reduced with a low retention time, while high retention times increased toxicity (Fig. 10). According to the results of the Microtox tests, toxicity in the anaerobic fermenter significantly decreased when low HRTs were used.

4. Conclusions

In conclusion, the two-stage anaerobic treatment process has significant advantages over single-stage anaerobic and aerobic biological treatments. High COD removal efficiency, significant colour removal and decreased toxicity of



Fig. 7. COD removal efficiency for both of the reactors at different HRTs.

the system are more effective in this two-stage process than in other wastewater treatment systems. Chemical and physical processes saw much more chemical use, electricity consumption and toxicity problems. A two-stage anaerobic reactor process can minimise these costs, and it is easily applicable as







Fig. 10. Toxicity at fermentation reactor in different HRT's.



Fig. 8. Gas compositions in the fermentation reactor at an HRT of 2 d: (a) SRT 10 and (b) 20.

a treatment. As can be shown from this study, the treatment of this kind of wastewater requires long HRTs in anaerobic biological systems, but a two-stage anaerobic treatment with short HRTs (up to 3 d) may be used effectively to treat this kind of wastewater.

Acknowledgements

The author would like to thank Istanbul University – Cerrahpasa support in the realization of the study.

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