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Adsorption and biological decolourization of azo dye Reactive Red 2 in semicontinuous anaerobic reactors

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Abstract

The microbial decolourization of Reactive Red 2 (RR2) dye has been studied under anaerobic conditions. Three semicontinuous bioreactors were operated with dye concentrations—R1 (control: 0 mg RR2 l^{-1}), R2 (100 mg RR2 l^{-1}) and R3 (200 mg RR2 l^{-1}). The parameters monitored were, oxidation–reduction potential (ORP), methane production, colour and chemical oxygen demand (COD) removal during the feeding cycles. The oxidation–reduction potential values for the first few days were above −150 mV, which later on decreased to less than −275 mV in all the reactors. Colour removal during the first few days of operation was due to adsorption of dye on to anaerobic biomass. However, under steady state conditions, colour removal was above 76% for both the dye containing reactors and it was due to biologically mediated degradation. Methane production and chemical oxygen demand removal in the control and dye containing reactors were almost the same. Integrated analysis of the monitored parameters indicated that, the primary mechanism of colour removal was adsorption of RR2 on to anaerobic biomass and subsequent degradation. Decolourization rates were found to be first order with respect to dye concentration, although an increase in the influent dye concentration resulted in a decrease in the rate from 0.0074 (g volatile suspended solid, VSS)$^{-1}$ h^{-1} (100 mg RR2 l^{-1}) to 0.0039 (g VSS)$^{-1}$ h^{-1} (200 mg RR2 l^{-1}). Based on total methane production no inhibition effect of dyes was observed but total methanogenic activity (TMA) results exhibited inhibition of methanogenesis.

Keywords: Azo dye; Adsorption; Degradation; Redox potential; Methanogenic activity

1. Introduction

Textile industry wastewater due to the presence of dyes is difficult to treat by traditional wastewater treatment technology. It is estimated that 280,000 t of textile dyes are discharged every year worldwide. Degradation of dyes, especially azo dyes which contribute to about 70% of all used dyes, is difficult due to their complex structure and synthetic nature [1]. Not only aesthetic problems occur due to dyes, but also biotoxicity and the possible mutagenic and carcinogenic effects of azo dyes have been reported [2]. The colour of dye affects photosynthetic activity in the water body. Further, the released dyes on degradation form toxic amines in sediments [3]. Although some of the dyes are adsorbed on to aerobic sludge in wastewater treatment plants the applied aerobic microbial process cannot readily remove it from wastewater [4]. Additionally the dye reduces the treatment efficiency in these plants [5], which may lead to a collapse of the biological treatment facility. Therefore physico-chemical or physical methods have been investigated to overcome the aforementioned problems. The physico-chemical methods have the limitations of high operational costs and generate large quantity of sludge for disposal. Biological treatment of dyes seems to be a cost effective alternative to the physico-chemical methods. While azo dyes and especially reactive azo dyes are not degradable aerobically, decolourization of azo dyes can be achieved under methanogenic conditions [6,7]. The reductive cleavage of the azo bond of the dyes was investigated under the reducing atmosphere in anaerobic reactors and batch assays. The products basically aromatic amines were found to be more toxic than the actual dyes [1,7]. Therefore further treatment of the effluent is necessary.

Reactive azo dye Reactive Red 2 (RR2) was chosen for this study, because it is widely used for dyeing cellulosic fibres. Only 60–70% of the reactive dye reacts with the fibre

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during the dyeing process, the remainder is hydrolyzed and is released in to the environment. Beydilli et al. [8] studied the biological decolourization of RR2 under aerobic, anoxic and methanogenic conditions using batch reactors. The dye was not decolourized under aerobic conditions but 92% decolourization was obtained under anaerobic conditions.

Most of the earlier studies on anaerobic decolourization have focussed on a few significant parameters, such as, colour and chemical oxygen demand (COD) reduction or colour removal and methane production and their significance and correlation is not clear. There is a need to examine the underlying process of anaerobic decolourization. Therefore in this work various significant parameters have been monitored and their correlation is studied. Further, most of the reported kinetic studies on anaerobic biological decolourization used unacclimatized [8] or improperly acclimatized sludge. Thereby adsorption and biologically mediated degradation phenomenon would occur simultaneously and may lead to erroneous estimation of decolourization kinetic constant values. Therefore in this study the variation of all parameters was studied during the start-up phase and when the quasi-steady state conditions were achieved and also it was ascertained that decolourization was occurring due to biologically mediated degradation, then only kinetic studies were conducted. Beydilli et al. [9] and Carliell et al. [6] assessed the toxicity of dyes on the anaerobic biomass, using a maximum rate ratio (MRR) method as suggested by Owen et al. [10]. However, in the present study a comparison between MRR and total methanogenic activity (TMA) test [11] has been done to determine the toxicity of dye on to the biomass.

2. Materials and methods

Commercial grade dye RR2 was obtained as water-soluble powder from the local market and used for the study without any further purification. The chemical structure of the dye is shown in Fig. 1.

2.1. Inoculum

The anaerobic sludge obtained from a full-scale Upflow Anaerobic Sludge Blanket Reactor (UASB) treating dairy wastewater (Mahananda Dairy, Goregaon, Mumbai, India) was used as an inoculum for the semicontinuous (batch-fed) reactors. After 3 days of storing at room temperature to reduce the organic matter from the dairy process the total suspended solids (TSS) and the volatile suspended solids (VSS) were measured. The sludge was flocculent in nature and contained an initial TSS and VSS of 20.2 and 12.5 $g\,l^{-1}$, respectively. All the bioreactors were seeded with same amount of sludge so as to obtain an initial VSS concentration of 4.4 $g\,l^{-1}$ as indicated in Table 1.

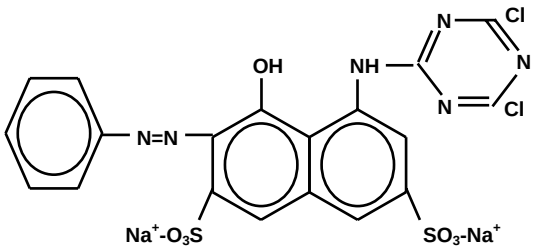

Fig. 1. Chemical structure of Reactive Red 2.

2.2. Feed wastewater

The feed wastewater was prepared by simulating dye bath effluent. It was prepared as described by Willetts et al. [12]. Stock starch solution (18.7 $g\,l^{-1}$) was prepared by heating for 2 h at 100 °C. To this solution 28.05 g sodium bicarbonate was added. The stock dye solution (10 $g\,l^{-1}$) was prepared by adjusting the pH of solution to 11 using 0.5 M NaOH and then heating the solution at 80 °C for 2 h. The influent feed mainly contained in $g\,l^{-1}$: starch, 1.87; $NaHCO_3$, 2.805; NH_4Cl, 0.58; KH_2PO_4, 0.23. The trace element solution 3 $ml\,l^{-1}$ was added to the feed wastewater, consisting of the following chemicals in $g\,l^{-1}$: H_3BO_3, 0.05; $FeCl_3$, 2.00; $MnSO_4$, 0.5; $CuCl_2{\cdot}2H_2O$, 0.03; $(NH_4)_6Mo_7{\cdot}4H_2O$, 0.05; $AlCl_3{\cdot}6H_2O$, 0.05; $CoCl_2{\cdot}6H_2O$, 2.00; $MnCl_2$, 0.25; $MgCl_2$, 1.00; EDTA, 0.05; $NiCl_2{\cdot}6H_2O$, 0.25; Yeast extract, 1.0; concentrated HCl, 1 ml.

2.3. Experimental set-up and reactor schedule

The experiments were carried out in dark brown glass bottles to avoid photocatalytic degradation of the dyes due to photo oxidation processes. The gases produced were passed through a NaOH solution. Only methane passed through and both carbon dioxide and hydrogen sulphide were trapped. The methane displaced NaOH solution from the gas trap and the volume of displaced solution was equivalent to the volume of methane. The produced methane was measured after 24 and 48 h. The experimental set-up is shown in Fig. 2.

The bioreactors were operated under different aqueous phase conditions as mentioned in Table 1. The control reactor contained only starch, nutrients and trace elements. The

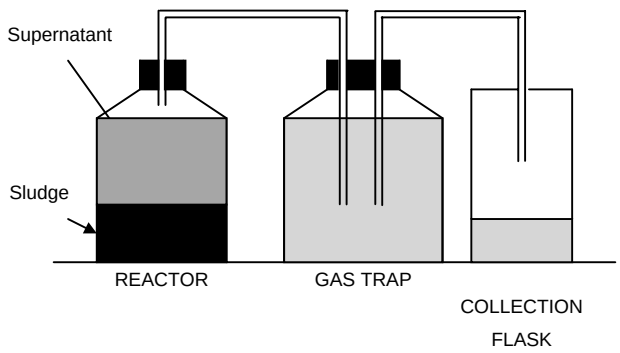

Fig. 2. Schematic of the experimental set-up.