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Anaerobic and Hydrogen Peroxide Decolourisation of Azo Dyes : A Comparative Evaluation

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Abstract

Efficient decolourisation of azo dyes by anaerobic biological process and chemical oxidation (ozone, Fenton and H_2O_2) process has been chaimed by both the methods. A comparative evaluation of chemical oxidation (H_2O_2 and Fenton's reagent) and anaerobic process for their efficacy for azo dye decolourisation has been done. Azo dyes namely, Orange-II (C.I. Acid Orange 7), Reactive Blue-H3R (C.I. Reactive Blue 13), Reactive Red-HE7B (C.I.Reactive Red 141) and Reactive Black-3HN (C.I.Reactive Black 8) were selected for the study. Anaerobic decolourisation experiments were conducted for a period of more than 50 days with a hydraulic retention time (HRT) of 10 days and at ambient temperatures. Oxidative decolourisation studies were conducted with varying peroxide dosage of 1.5 to 50 mM H_2O_2 concentrations. Decolourisation efficiencies achieved during anaerobic process was more than 99% for all the dyes evaluated. In case of hydrogen peroxide (50 mM H_2O_2 conc.) treated dye solutions, decolourisation efficiencies observed were 37, 12, 5 and 10% for orange, blue, red and black dye respectively. Fenton's reagent (Fe(II) + 50 mM H_2O_2) achieved 99 % decolourisation for dyes Orange-II and Reactive Blue-H3R. Therefore it seems that anaerobic process would be economical for decolourisation of azo dyes in comparison to chemical oxidation processes.

Introduction:

Wastewaters from a textile industry contain dyes, sizing agents, dyeing aids, etc and therfore are characterized by their deep color and high concentrations of environmental pollutants. Azo dyes constitute the largest and most varied group of synthetic organic dyes in use today. Due to the poor exhaustive properties of azo and reactive deys, as much as 30% of the initial dye applied remains unfixed and ends up in effluents[1]. Some of these dyes and/or dye degradation products are proven to be carcinogens and mutagens. Various treatment methods such as physicochemical, advanced oxidation processes, biological processes and usually in a combination is applied to treat textile wastewaters to the discharge limits and disposed off[2]. Advanced oxidation processes are reliable, robust but are uneconomical. Whereas, investment costs for biological processes are 5 to 20 times less than chemical ones such as ozone or hydrogen peroxide. Meanwhile treatment costs range from 3 to 10 times less[3]. Due to the electron withdrawing nature of the azo dyes/ bonds they are not susceptible to oxidative catabolism hence are not removed during the aerobic treatment[4]. However, under anaerobic conditions, decolourisation of azo dyes and reactive dyes can be easily achieved[5]. Most of the earlier studies have focussed on decolourisation by either anaerobic treatment or chemical oxidation, and are claimed to be superior over each other[6,7,8,9]. A comparative evaluation of anaerobic process and chemical oxidation would facilitate the choice of the treatment technology. In this paper a comparative evaluation of decolourisation of four azo dyes by semicontinuous anaerobic mixed bacterial cultures and hydrogen peroxide has been done.

Materials and Methods:

Commercially important azo dyes were purchased from the local market. They were used for the studies without any purification. Major characteristics of the dyes used are summarized in the Table 1. Seed sludge to the reactors was collected from the primary settling tank of the domestic sewage treatment plant of I.I.T Bombay, Powai, Mumbai, India.

Table 1–Characteristics of dyes

Dye	λ_{max} (nm)	COD (mg/L) For dye conc. = 1000 mg/L	Chemical Structure (Reference)
Orange II	480	1280	10
Reactive Blue H5R	597	360	-
Reactive Red HE7B	543	560	5
Reactive Black 3HN	588	600	11

Experimental set-up and procedure

Anaerobic degradation studies using selected azo and reactive dyes.

Semi-continuous studies on anaerobic degradation using selected azo and reactive dyes were conducted using 5-L glass aspirator bottles. Each reactor was filled with 1-L of sludge (TS: 70 and VSS: 30g/L). The ractors were fed the simulated cotton dyeing effluent prepared according to the procedure outlined in O'Neill et al[12]. More details regarding the feeding procedure is described elsewhere[7]. Initial dye concentration used for the studies was 100 mg/L. Influent pH was in the range of 7.0 to 7.2. Influent alkalinity was in the range of 84-1140 mg/L. Organic loading rate and sludge loading maintained in the reactors were in the range of 0.008-0.216 kgCOD/m^3.d and 0.010-0.036 kgCOD/kgVSS.d respectively.

Decolourisation of influent dye solutions using hydrogen peroxide:

The experiments were conducted using 1L glass beakers at room temperatures (32.35°C). Studies were conducted for varying hydrogen peroxide dosages of 1.5 to 50 mM concentrations. Reactions were conducted for a period of 24 hours. Absorbance values at different λ_{max} values at predetermined time intervals were recorded. Initial pH of the dye solutions was 7.0-7.2.

Analytical methods: Total alkalinity, Chemical oxygen demand (COD: closed reflux titrimetric method), Total solids (TS), MLVSS (Mixed liquor volatile suspended solids) were measured according to the procedure outlined in Standard Methods[13]. The other details are given in Manu and Chaudhari[7].

Results and discussion:

Semi-continuous reactors were operated to simulate the continuous rectors, as it is easy to assess and elucidate biodegradation of any compound in a semi-continuous mode rather than the batch mode. Therefore anaerobic degradation of selected reactive and azo dyes under semi-continuous conditions was conducted.

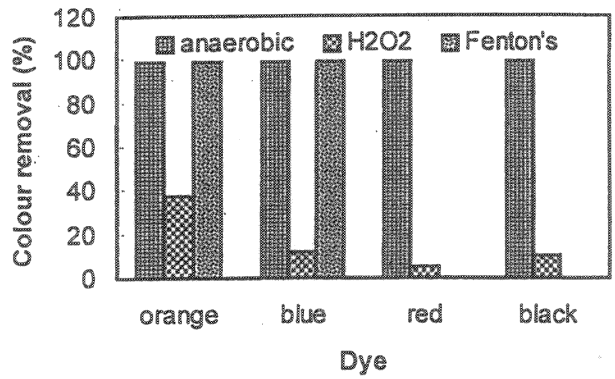

Figure 1 : Colour removal efficiencies observed during anaerobic, hydrogen peroxide and Fenton's treatment of the selected azo dyes.

As seen from the Figure 1 during anaerobic decolourisation studies, colour removal of upto 99% could be achieved for all the dye containing reactors. In case of decolourisation studies using hydrogen peroxide, colour removal of up to 37, 12, 5 and 10% could be achieved for orange, blue, red and black dyes for a peroxide dosage of 50 mM (2000 mg/L) concentration and for a reaction period of 24 hours. Fenton's reagent achieved 99% decolourisation in 30 minutes for Orange-II and Reactive Blue-H3R, though the decolourisation efficiency of Fenton's reagent is high but it generates significant amount of sludge, which might create disposal problems. During anaerobic metabolism, dyes were transformed to their corresponding aromatic amines as observed in their respective effluent UV-Visible absorbance spectra (figures not shown). Hence during anaerobic metabolism the dyes are reductively cleaved, breaking the azo bond, thus decolourising the dye molecules. Low ORP values (reducing conditions) probably due to conversion of sulfates to sulfides prevailing inside the bioreactors could also have decolourised the dye molecules. Also the extent of decolourisation was independent of chemical structure of the dye. There was no significant change in the absorbance spectra of the effluent solutions during peroxide treatment. The decolourisation efficiencies observed during peroxide treatment seemed to depend upon the chemical structure of the dye to a certain extent. The dye which was having a relatively simpler structure, less number of azo bonds and the sulfonic groups seemed to be decolourised effectively than the dyes which had complex chemical structures and more number of sulfonic group substituents.

Conclusions:

The selected azo dyes could be easily decolourised under the anaerobic conditions employed in this study. Colour removal of more than 99% could be achieved for all the selected dyes. Whereas, peroxide process at 50 mM could only achieve decolourisation from 5 to 37% and Fentons reagent achieved 99% decolourisation of Orange-II and Reactive Blue-H3R. Comparative assessment indicates that anaerobic biological process is more efficient and possibly economical than the chemical oxidation processes evaluated.

References

1. O'Neill, C, Hawkes F., R., Hawkes, D., L., Lourenco, N., D., Pinheiro, H., M and Delee, W., 1999. Colour in Textile Effluents - Sources, Measurement, Discharge Consents and Simulation: A Review. J. Chem. Technol. Biotechnol: 74:1009-1018.

2. Banat, I., M., Nigam, P, Singh, D and Marchant, R., 1996. Microbial Decolorization of Textile-Dye-Containing Effluents:

A Review. Bioresource Technology: 58: 217-227

3. Mario, A, Esplugas, S, and Saum, G., 1997. How and Why Combine Chemical and Biological Processes for Wastewater Treatment. Wat. Sci Technol. : 35(4): 321-327.

4. Knackmuss, H., J., 1996. Basic Knowledge and Perspectives of Bioelimination of Xenobiotic Compounds. Journal of Biotechnology: 51(4): 287-295.

5. Carliell, C., M., Barclay, C., J., Naidoo, N., Buckley, C., A., Mulholland, D., A and Senior, E., 1995. Microbial Decolourisation of a Reactive Azo Dye under Anaerobic Conditions. Water SA: 21(1): 61-69.

6. Nigam, P, Banat, I.M., Singh, D and Marchant, R., 1996. Microbial Process for the Decolourisation of Textile Effluent Containing Azo, Diazo and Reactive Dyes. Process Biochemistry: 31(5): 435-442.

7. Manu, B and Chaudhari, S., 2002. Anaerobic Decolorisation of Simulated Textile Wastewater Containing Azo Dyes. Bioresource Technology: 82 (3): 225-231.

8. Arslan, I, 2001. Treatability of a Simulated Disperse Fye-Bath by Ferrous Iron Coagulation, Ozonation, and Ferrous Iron-Catalyzed Ozonation. Journal of Hazardous Materials: B85: 229-241.

9. Spadaro, J.T., Isabelle, L and Renganathan, V, 1994. Hydroxyl Radical Mediated Degradation of Azo Dyes: Evidence for Benzene Generation. Environ. Sci. Technol.: 1389-1393.

10. Zee, F.,P.,V., Lettinga, G and Field, J.,A., 2000. The Role of (Auto) Catalysis in the Mechanism of an Anaerobic Azo Reduction. Wat.Sci. Technol: 42(5-6): 301-308.

11. Feng, W., U., Nansheng, D and Helin, H, 2000. Degradation Mechanism of Azo Dye C. I. Reactive Red 2 by Iron Powder Reduction and Photooxidation in aqueous solutions. Chemosphere: 41(8): 1233-1238.

12. O'Neill, C., Hawkes, F., R., Hawkes, D., L., Estves, S and Wilcox, S., J., 2000. Anaerobic-Aerobic Biotreatment of Simulated Textile Effluent Containing Varied Ratios of Starch and Azo Dye. Wat. Res.: 34 (8): 2355-2361

13. APHA, 1989. Standard Methods for the Examintion of Water and Wastewater. 17th Edition, American Public Health Association, Washington.

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