Photocatalytic degradation of naphthol ASBS dye over TiO$_2$-based catalysts

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The photo-assisted degradation of naphthol ASBS dye has been carried out using a batch reactor. TiO$_2$, bare and immobilized over ceramic beads, metal ion doped samples of silver, copper, tin and montmorillonite clay on titanium dioxide have been used for the degradation studies. The investigations were made on the basis of the chemical oxygen demand (COD), total organic carbon (TOC), UV-visible absorption and reflectance spectroscopy measurements. The focus of the study is on the prospects of photocatalytic dye degradation methods which provide a new approach for the treatment of dye pollutants in waste water.

Colour sells textiles and the demand for textiles is ever increasing. Textile wastes are generally coloured, highly alkaline and high in biological oxygen demand (BOD). Large amounts of dyes generated as effluents from dyeing industries have become a focus of environmental remediation efforts. Some physico-chemical approaches such as coagulation, sedimentation, bleaching, ion-exchange on synthetic adsorbent resins, adsorption over activated charcoal, chemical treatments, ozonation etc. provide partial solutions to the treatment problems of dye industry effluents. Dyes are particularly difficult group of compounds to treat, as they are diverse. Thus, all the conventional methods are expected to be significantly harder than simple photocatalytic technique for dye and dye intermediate degradation as reported recently in the literature$^{1,2}$ for acid orange, naphthalene blue black, and alizarin red S etc. Naphthol ASBS (N-ASBS) with scarlet RC is used extensively in colouring Indian Saries to get red colour of the fabrics. The present study shows the photocatalytic degradation of N-ASBS dye over TiO$_2$-based catalysts.

Experimental

The catalysts used in our study are titanium dioxide (P-25 Degussa brand) as such and bare TiO$_2$ immobilized on ceramic beads of 2-8 mm size. The precursor salts used for doping TiO$_2$ were in the form of chlorides, nitrates and sulphates of copper, silver, tin and also montmorillonite clay. The dye N-ASBS obtained from M/s Sandoz India Ltd. was used as such. The structure of N-ASBS is shown below (1).

![Structure of N-ASBS](image)

Aqueous solution of the dye ($=0.1$ wt %) of 200 ml solution was used in each run. The reactors were kept under sunlight for illumination. The processes of degra-
Results and discussion

Preliminary experiments on the photo-catalyzed reduction of N-ASBS in aqueous suspensions, established that the colour gets bleached with sunlight illumination. The photo-degradation profiles in Fig. 1A represent the changes in COD, TOC measurements, at time intervals of 6 h for a N-ASBS sample containing 0.1 wt% solution with 500 mg P-25 titania. The effect of catalyst immobilization over ceramic beads on the COD, TOC values (Fig. 1B) is more than that on the bare one, but the incremental value appears to approach a constant value.

The characteristic colour of the dye quickly disappeared in bare and immobilized titania over ceramic bead samples. This is evident from the bleaching of the dye within one hour. Complete colour bleaching from yellow occurs within 1 to 2 h depending on the sunlight illumination. As we continued the illumination the COD, TOC measurements were monitored with time. The blank experiment results showed that the simultaneous presence of photo-catalyst is necessary along with light and electron acceptor, i.e., oxygen. In a series of experiments, the effect of metal dopant over P-25 titania was also examined and the results obtained for N-ASBS dye over these catalysts show that the effect is small as is evident from Fig. 1C. The photo-degradation of TiO$_2$ doped samples with Cu, Ag, Sn and montmorillonite clay did not work in the positive direction.

The absorption spectra of the N-ASBS with and without photocatalytic treatment are shown in Fig. 2. In this study we have utilized the disappearance of the absorption band to monitor the decolourization process. These changes in absorption indicate that an interaction occurs between N-ASBS and TiO$_2$ which changes the electronic state of N-ASBS rendering it colourless. There is a need for examination of various control experiments for an in-depth study. The reflectance spectra of the powders were also recorded because of the following reasons. The most important issue in the photo-catalyzed mineralization of N-ASBS dye substrate is whether the dye colour in solution is getting bleached or the dye is getting deposited over the catalyst. This point was checked from the reflectance spectrum of the recovered TiO$_2$ powder after illumination. It was found more or less equivalent to that of unused sample as shown in Fig. 3B (3). Similarly, the degradation of N-ASBS was found to proceed in a similar way with montmorillonite doped samples of TiO$_2$. The N-ASBS dye adsorbed over TiO$_2$ powder catalyst also sheds its colour slowly after a few hours of illumination by sunlight. This shows that the photocatalytic degradation of N-ASBS dye may be a viable method for the safe disposal of the waste water containing this dye. With suitable modifications in the
for practical application, it is also necessary to analyze the decolourized state of organic dye in order to couple this technique with bio-remediation. More detailed investigation is currently under progress.

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References


Fig.3 - (A) Reflectance spectra of (1) TiO2, (2) used catalyst of 3A - 1, (3) 3 A - 1 doped with 3 wt% montmorillonite and (4) used catalyst of 3A - 3; (B) (1) Catalyst 3A - 1, (2) catalyst 3B - 1 with dye impregnation and (3) catalyst 3B - 2 after illumination and (C) (1) catalyst 3A - 3, (2) catalyst 3C - 1 with dye impregnation and (3) catalyst 3C - 2 after illumination.