

# **Oxidation of Colors**

## How can oxidation be done

Synthetic dyes are difficult to degrade due to their complex aromatic structure and synthetic origin. Some of them are known to be toxic or carcinogenic

The oxidation of dyes from colored textile dye containing wastewater by activated carbon (AC)/hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) will be discussed. **Acid Red 18 (AR18)**, **Direct Red 80 (DR80)** and **Reactive Red 194 (RR194)** have been taken as model dyes.

Dye oxidation by AC/ $\text{H}_2\text{O}_2$  was studied by UV–Vis spectrophotometer and Ion chromatography (IC).

The effects of AC dosage, initial dye concentration, pH and salt on dye oxidation were evaluated. Kinetics analysis indicated that the dye oxidation rates could be approximated at pseudo-second order model.

## How does the oxidation happen

Combination of both adsorption and heterogeneous catalysis into a single process could offer an attractive alternative in the dye oxidation treatment. Due to the complex role of AC, the catalytic decomposition of  $\text{H}_2\text{O}_2$  and contaminants with AC deserves further investigation

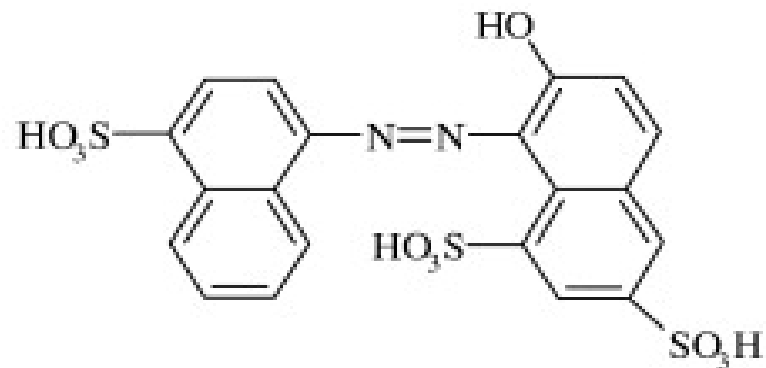
The catalytic decomposition of  $\text{H}_2\text{O}_2$  by AC involves the exchange of a surface hydroxyl group on AC surface with a hydrogen peroxide anion ( $\text{HO}_2^-$ ) to generate peroxide on the surface. The AC active site is regenerated by decomposition of  $\text{H}_2\text{O}_2$  molecule to oxygen

## Oxidation conditions for Dyes

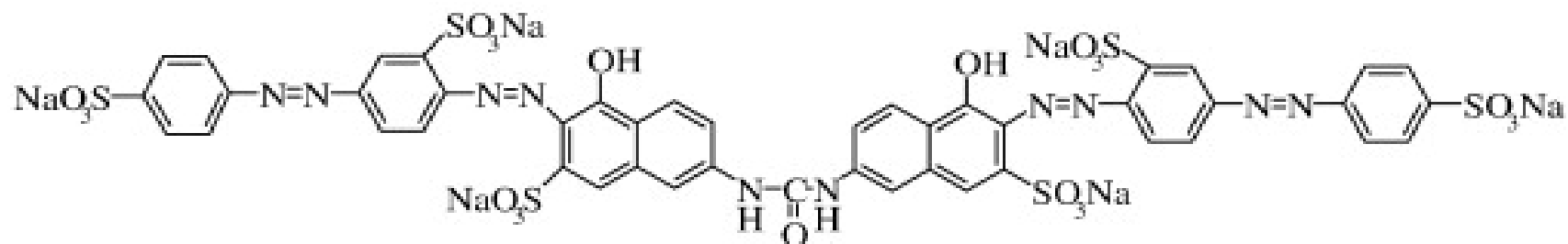
The dye oxidation experiments were conducted by mixing various amounts of AC (0–0.35 g/L) in jars containing 400 mL of a dye solution (50 mg/L) and  $\text{H}_2\text{O}_2$  (0.41 mM) at various pH (2.5–10) and agitation speed of 200 rpm and 25 °C. The solution pH was adjusted by adding a small amount of  $\text{H}_2\text{SO}_4$  or NaOH.

The samples were withdrawn from the solution at regular time intervals and the reaction was blocked by addition of methanol. The suspensions were centrifuged by Hettich EBA20. The change on the absorbance at maximum wavelength ( $\lambda_{\text{max}}$ ) of dyes (509 nm for AR18, 543 nm for DR80 and 513 nm for RR194) was monitored by UV–Vis spectrophotometer (Perkin-Elmer Lambda 25).

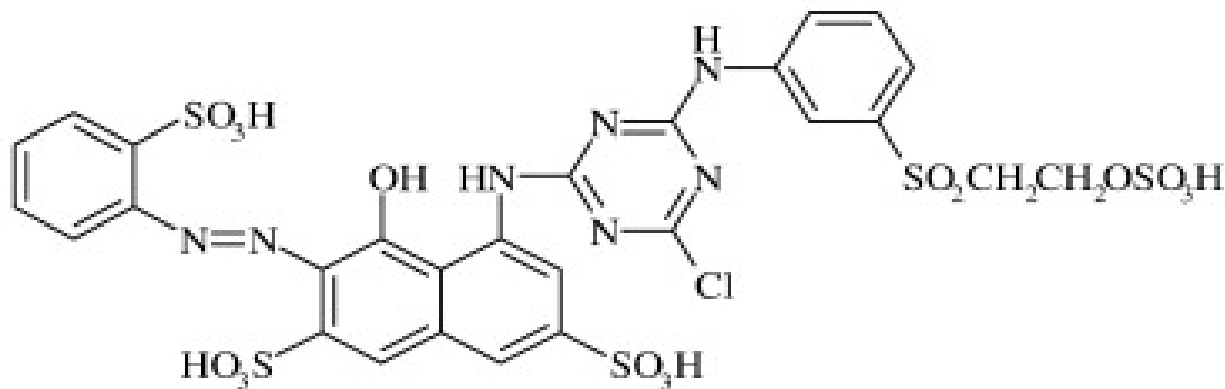
**Acid Red 18 (AR18),      Direct Red 80 (DR80) and      Reactive Red 194 (RR194)**



**a**



**b**



**c**

## Reaction Conditions

- To investigate the effect of AC dosage on dye oxidation, different amounts of AC (0, 0.05, 0.15, 0.25 and 0.35 g/L) were applied to the reactor containing 400 mL dye solution (50 mg/L) and  $\text{H}_2\text{O}_2$  (0.41 mM) using jar test at room temperature (25 °C) and pH 2.5 for 60 min.
- The effect of initial dye concentration on the percentage of dye oxidation was studied by adding optimum amount of AC (0.1 g for AR 18, 0.06 g for DR80 and 0.06 g for RR194) to 400 mL of different dye concentrations (25, 50, 150, 250 and 350 mg/L) and  $\text{H}_2\text{O}_2$  (0.41 mM) at pH 2.5.
- The effect of different pH values (2.5, 5–5.5, 7 and 10) on dye oxidation was investigated by contacting 400 mL of dye solution (50 mg/L),  $\text{H}_2\text{O}_2$  (0.41 mM) and optimum amount of AC for each dye.
- For investigating the effect of salt on the percentage of dye oxidation, 0.02 M of different salts ( $\text{Na}_2\text{SO}_4$ , NaCl,  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ ) was added to 400 mL of dye solution (50 mg/L) and  $\text{H}_2\text{O}_2$  (0.41 mM) with optimum amount of AC at pH 2.5.

# Carboxylic acid intermediates of dye oxidation

- During the oxidation of dyes, various organic intermediates were produced. Consequently, destruction of the dye should be evaluated as an overall oxidation process, involving the oxidation of both the parent dye and its intermediates.
- Further hydroxylation of aromatic intermediates leads to the cleavage of the aromatic ring resulting in the formation of oxygen-containing aliphatic compounds. Formate was detected as important aliphatic carboxylic acid intermediate during the oxidation of dyes. Carboxylic acids can react directly with reactive species such as hydroxyl radicals generating  $\text{CO}_2$ .

The oxidation with  $\text{H}_2\text{O}_2$  in the absence of activated carbon and the adsorption of dyes on activated carbon present a low performance for dye removal from solutions. The synergistic effects of AC and  $\text{H}_2\text{O}_2$  were observed because of the catalytic performance of AC for decomposition of hydrogen peroxide into hydroxyl radicals. The results showed that the kinetics of dye oxidation at different operational parameters followed second order kinetic model. This means that dye oxidation depends on both hydrogen peroxide and AC. It can be concluded that the AC/ $\text{H}_2\text{O}_2$  could be used as an eco-friendly material to remove dyes from colored wastewater.

## Nanoceria as Oxidant for dyes

- Nanoceria is a nanoparticulate oxidizing agent in the oxidations of the organic dyes.
- Investigated on the oxidations of organic dyes in pH 4.0 citrate buffer in the presence of nanoceria. Upon mixing nanoceria with organic dyes in the citrate buffer, for example dopamine, 3,3',5,5'-tetramethylbenzidine (TMB), and 2,2-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) (AzBT), distinct color changes were observed within minutes, implying that oxidations of the dyes occur in the solutions. And the kinetics can be described by the Michaelis–Menten model.

Based on these observations, nanoceria was postulated as being oxidase-like.

# **Oxidation of dyes by manganese tetraphenyl porphyrin activated peroxy bleach**

The oxidation of a number of dyes in predominantly aqueous systems by Tetra-phenylporphyrinato manganese(III) imidazole, MnTPP(Im), activated peroxy bleach has been studied. Dyes with an olefinic linkage in the chromophoric group are readily oxidized by perborate even in the absence of the activator.

On the other hand, dyes with an azo linkage are resistant to oxidation and are bleached only to a limited extent (25%) even by MnTPP(Im) activated perborate. In the presence of a surfactant, alkylbenzene sulphonate, bleaching is further inhibited by micellar solubilization of the dyes. Sulphonation of MnTPP(Im) only marginally improves the bleaching efficiency in presence of the surfactant. MnTPP(Im) is also destroyed by perborate in the absence of the substrate. In view of these limitations, the metalloporphyrin activated peroxy bleach system is not promising for application in detergent systems. Attempts have also been made to explain the difference in the behaviour of different substrates on structural consideration