Wastewater Treatment of Dye Intermediate Industry

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ABSTRACT

The aim of this study is to examine and compare the treatment performance of alum, ferrous sulfate, and ferric chloride in dye intermediate wastewater at different dosage. COD, TDS and pH. It was observed that wastewater generated by the dye intermediate industry is highly acidic with dark colour contain high TDS and high organic load with refractory constituents. Jar tests were conducted using alum, ferrous sulfate, ferric chloride as coagulants for chemical treatment. It was found that ferric chloride is the most effective coagulant. This chemically treated sample was further chlorinated with calcium hydrochloride. The significant reduction was observed in colour of the treated effluent. The above results confirmed the effluent standards for COD, pH and colour but standards for TDS could not be achieved, which requires further investigations.

Key words: Dye, β-naphthol, COD, TDS, Colour, pH, Treatment.

Introduction

2-naphthol also known as β-naphthol, B-naphthol, is an important organic chemical raw materials and dyes intermediates, mainly used in dyestuff, organic pigments, rubber antioxidant, as well as pharmaceutical and pesticide industries. Dye Allied Industries is the fourth largest manufacturing in the country and accounts for 10% of GNP valued at Rs. 20,000 crores per annum. A large variety of dyestuffs are produced in the country. These include basic dyes, reactive dyes, dyes for food industries, optical whitening agents for polyester fibre, special leather dyes and dye intermediates. The production of dyestuffs and their intermediates in the country is mainly a development of post independence era in India about 321 units in organised sectors produces dyes and dye intermediates spreading in 13 states and 2 union territories. In country about 16 classes of dyes are produced Mooning et al. (1980). The industries manufacturing dyes, dye intermediates, dyestuffs are responsible for pollution of receiving water body on account of their high toxicity, colour, organic nature, chloride content etc. All these impurities cause severe environmental pollution if waste is discharged untreated. In view the pollutional potential, the dye intermediate waste water will have to be adequately treated prior to its disposal, with the enforcement of water pollution control laws, dye intermediate manufacturing industries are required to make provisions for wastewater treatment and disposal of sludge. Dye released to the waste stream, if without proper treatment, could exert great impact to the environment. Hence, for protecting the environment and to meet the stringent government law, many researchers try to find an effective and economical way of dye-containing wastewater treatment. Several studies have been performed on three categories. They are chemical, physical, and biological methods. The oxidation agents used in practice or in research project (removal residual colour) are chlorine, or hydrogen peroxide and the later usually together with iron (II) sulfate (Fentons reagent), ozone, or UV irradiation. Heikkilä et al. (2000), degraded some azo dye to decolorize using lignin peroxidase isoenzyme. They found that azo dye (certain) degraded to some extent and ability to degrade varied between lignin peroxidase isoenzymes and optimum pH for decolorization differed among dye. Lin and Liu (1994) used combination of ozonation and coagulation for treatment textile wastewater. It is shown that ozonation effectively remove complete decolorization of textile wastewater in less than 10 minutes in the continuous reactor. Also, coagulation removed dissolved and suspended solids with a COD removal efficiency of up to 66%. Even though dyes are difficult to be degraded biologically, many researchers interested in dye-containing wastewater. Buys and Bell et al. (2000) treated and decolorized dye-wastewater using an anaerobic baffled reactor. It reduced in COD of 50 – 60% and colours of about 95%. In addition, physical chemical processes, for example chemical coagulation, active-carbon adsorption, and ozone oxidation studies showed that the decrease of COD and colour for dye wastewater was not efficient. These above-mentioned processes could not completely treat the dye wastewater. Lastly, flying ash was investigated Viraragahan, T., and K.R. Ramakrisna (1999): for its ability to absorb dyes from aqueous. Batch pH, kinetics and isotherm studies were performed in laboratory scale with synthetic dyes. Four concentrations of solution with different compositions and particles size were treated with fly ash (granular activated carbon) and the results exhibited reasonably good synthetic dye
removal. Shirazi et. al. (1977) in Iran investigated first time treatment for dye wastewater. They found that the coagulation with ferric chloride reduces COD by 51% and colour by 68%. Inclusion of activated sludge treatment increases the overall reduction of both COD and colour to 75%. Thomas Crowe et al reported that colour from dispersed dyes can be removed by coagulation with cationic polymers and also with alum. Fison Ltd. (1976) found success in removal of colour and COD with magnesium salt as coagulant. Endysuskin et.al.(1979) reported that chlorine and sodium hypochlorite are effective in decolourising some dyes and have been used for treatment of effluents from the production of dyes. Taran et.al.(1975) studied the reaction of 1-naphthol with chlorine and ozone in dilute aqueous solution found that chlorination of 1-naphthol gives pentachlorotetralene and ozonation at 5-20 mg/L decomposes into phenolic acid and oxalic acid. Mitsui (1981) used nitratosing and ferric salt for treatment of wastewater with naphthols and observed that the treated effluent thus become free from detectable amount of naphthol. Raudseep and Raudseep (1967) reported that the removal of naphthol has increased with pH increase. Removal further found to be enhanced significantly in the presence of magnesium and phosphate and also reported that the thermal degradation of naphthol in gaseous H2O at 850 and obtain Indane and small amount of naphthelene as product of thermal degradation. Kantawala Deepak et.al. (1980) studied the treatability of dye wastewater with magnesium oxide and found 33.3% removal of COD Moning et.al. (1980) carried out treatability studies on wastewater from chemical manufacturing process. The wastewater containing naphthols are treated with NaNO2 solution, sulfuric, ferric chloride and ammonium hydroxide and allowed to settle. Effluent thus treated do not contain detectable amounts of naphthol Andrej et.al. (1965) used silica gel for removal of 2-naphthol, it is observed that 1-naphthol is absorbed on silica gel more strongly then 2-naphthol. Jorgenson (1974) the use of coagulation with alum and sedimentation by ion exchange as means of treating effluent. Coagulation was with 500 mg/lit alum, the pH being adjusted to 6 with caustic soda. After 2 hrs of settlement, the waste water was still coloured and was passed through a cellulose based cation exchanger and anion resin. The first bed also acted as a filter. Carbon dioxide was added prior to cation exchanger and to final effluent in order to maintain the pH value in the range 6-8. COD was reduced by 90-95% and the recovered water was coloured and was recycled for 5 times for dyeing without any detrimental effects. Anon (1977) emphasize the need to reduce the waste water volume as low as possible and maintain concentration as high as possible - not only to reduce cost to also to make treatment possible. These studies compared treatment of cotton finished waste by number of processes including coagulation and sedimentation or flocculation, adsorption on activated carbon, catalytic oxidation, activated sludge and ozonation. Coagulation and sedimentation had the disadvantage of producing voluminous quantities of sludge. Adsorption required pretreatment and reduces COD by 50% only. Catalytic oxidation also required pretreatment and was found to be not very effective or reliable. The recommended treatment for effluent not containing chromium or sulfide was activated sludge including a small dose of alum. Expected reduction of COD was 80% and BOD 90%. Residual colour removal would require and additional stage such as ozonation.

The main objective of this work was to investigate removal of colour TDS and COD by using alum, ferrous sulfate, and ferric chloride

Materials and Methods

The present studies were undertaken to quantify the discharge pattern and characterize the wastewater generated in the manufacturing process of typical dye intermediate industry. Studies were also undertaken for treatability of wastewater in the laboratory to explore the possible, economically viable treatment alternative to bring down the current pollution potential of waste water to the acceptable limits.

Characteristics of dye intermediate industrial waste water:

The samples characterized, were grab samples, as the system of production is batch wise. Table 1 shows the characteristics of typical dye intermediate industry.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1.36</td>
</tr>
<tr>
<td>Colour</td>
<td>Brownish black</td>
</tr>
<tr>
<td>TDS</td>
<td>2,85,000</td>
</tr>
<tr>
<td>COD</td>
<td>22,000</td>
</tr>
</tbody>
</table>

The variation in pH has profound effects on various treatment units/operations and secondly optimum pH is to be maintained for the safe disposal of the effluent to various receiving streams. Total Dissolved Solids are the potential parameter for designing of various units of treatment plants as well as crucial parameter for the effluent to be discharged in the drain, it has been analyzed. COD is to be analyzed for the organic potential of the wastewater, this parameter has been analyzed. It also finds significance in the standards for effluent to be discharged. Furthermore its analysis is quick. Colour standard recommended by various regulatory agencies are contradictory. Colour is not the criteria to accept the wastewater for influent standard it should be as faint as possible. But, to compare the reduction in colour, the colour has been monitored as %
transmittance by UV spectrophotometer at 420 nm wavelength. Although the concern of sulfate, BOD, and toxicity as major pollutants are not monitored due to the time consuming and instruments availability. In the experimentation pH adjustment was conducted as pretreatment.

**pH Adjustment**

Experiments were undertaken to asses the effect of different pH on removal of potential parameter viz. COD, solids etc.

**Methodology**

A magnetic stirrer with digital pH meter was used. 100 ml of wastewater sample was taken in a beaker and lime was added to get desired pH. Stirred the sample for sufficient time (10 minutes). The supernatant was siphoned out; filtered and potential parameters were monitored.

**Chemical Treatment Experiments**

For chemical treatment experiments, wastewater sample was taken. Coagulants viz. alum, ferrous sulfate and ferric chloride were used to analyze the effect on effluent by principle of chemical precipitation. Hydrated lime slurry was used for maintaining the required pH.

**Methodology**

Jar test apparatus was used for experiments for determining the optimum dose and optimum pH of each reducing agents. The apparatus consists of set of 4 beakers, having 1 lit capacity each. The arrangement is provided to add desired dose of the coagulant to the reactor units containing wastewater samples. Each reactor unit has mixing paddles. The mixing paddles are connected to driving motor with speed control provision through reducing gears. 500 ml samples of pretreated wastewater were placed into beakers. Removal efficiency of various parameters was observed for the coagulant. The respective coagulant doses tried were in the range, alum doses from 20-80 gm/L, ferrous sulfate doses from 40-100 gm/L, and finally for ferric chloride doses from 40-100 gm/L. During runs, the coagulation was achieved by rapid mixing at 100 rpm for 10 minutes and allowed to settle down for 60 minutes. Flocculation was not required as the wastewater contain high solid concentration. The supernatant was siphoned out, filtered and monitored for various parameters, viz., COD, TDS etc.

**Post Oxidation by chlorine**

Partially chemically treated wastewater sample was post oxidised by chlorination using oxidant calcium hypochlorite (commercial grade with 30% available chlorine).

**Methodology**

Experiment was carried out on wastewater treated with most effective coagulant. Sample was taken in a beaker and oxidant at varying dose from 25 gm/L to 100 gm/L was added, stirred for few seconds, and detained, for 12 hrs. The supernatant was siphoned out, filtered and monitored for COD, solids and % transmittance.

**Results and Discussions**

All treatability studies were done on concentrated mother liquor in batch reactors at laboratory scale as pretreatment, chemical treatment and post oxidation.

**Pretreatment**

The pH adjustment was conducted on raw wastewater and effect on removal COD and TDS was monitored.

**Effect of pH adjustment**

Polluting parameters were analyzed after raising pH to 6, 8, 10 and 12 of raw wastewater by adding appropriate quantity of lime. From table 5.2 it can be observed that maximum removal efficiencies were achieved at pH 12 i.e. 60% and 17.5% for COD and TDS respectively and thus leaving residual concentration of 14400 mg/L of COD and 235000 mg/L of TDS.

Fig. 1 shows the trend of decrease of residual COD and TDS with increase of pH. The probable reason for reduction of COD and TDS may be the precipitation of sulfate ions and some organic compounds present in raw waste water.

It has been also reported that for typical pharmaceutical industry waste water having initial pH 0.25, when treated with 1N NaOH resulted in about 73% removal of COD at pH 12.5 with no solid reduction.
Chemical Treatment

Three coagulants viz. alum, ferrous sulfate and ferric chloride were tried with pretreated sample. Effect on removal of COD and TDS were observed and analyzed after treatment for these coagulants. The initial values of the parameters of wastewater over which coagulation studies were undertaken are COD 22000 mg/L, TDS 285000 mg/L, pH 1.36 and percentage transmittance as 0.5% for all runs of jar test.

Table 2 to 8 indicates the results of treatability studies for the effect of dose of coagulants on the removal efficiencies of COD and TDS.

Alum as Coagulant

The data of table 2 and 3. indicates that optimum dose of coagulant is 40 mg/L at which the removal efficiency is observed for COD as 25% while that for TDS as 11.5%. On comparing with other coagulants it can be interpreted that alum is not a effective coagulant for present situation. When alum is used as coagulant phenomenon of adsorption cum co-precipitation takes place in the aqueous solution. Probable reason for removal of COD could be the co-precipitation/adsorption of organic impurities present in the waste water sample with floes of Al(OH)₃. Furthermore optimum pH is observed to be 7.5 which is in the favourable working range of 5-8 for alum. It has been also reported that for a typical textile industrial wastewater alum reduces COD upto about 44% (Lin and Liu, 1994).

Ferrous Sulfate as Coagulant

Coagulation runs for ferrous sulfate as coagulant indicate that maximum reduction in COD and TDS was achieved at dose of 80 gm/L and pH 8 i.e. 36% and 13.6% respectively. The reduction in COD may be due to precipitation by adsorption of organic impurities with the Fe(OH)₃ floes. Furthermore, it has been also reported that for a textile industrial wastewater ferrous sulfate reduces COD about 40% (Lin and Liu, 1994).

Ferric Chloride as coagulant

It has been observed from the data of table 6 and 7 that maximum reduction in COD and TDS was achieved at dose of 80 gm/L and pH 8 i.e. 73% and 20.3% respectively. The probable reason for reduction of COD could be the precipitation cum adsorption of organic impurities present in waste water with Fe(OH)₃ floes.

The variation of removal COD and TDS with different doses of three coagulants at various pH for respective optimum dose are depicted in Fig. 2 to 5. It is observed that the use of ferric chloride is effective in present situation. For further treatability studies, chemically treated (with FeCl₃) sample was taken having initial parameters viz COD 6000mg/L, TDS 227000 mg/L and percentage transmittance as 1.1%.

Post Oxidation

Experiments for these tests resulted in further reduction of COD and TDS. It can be observed from data that at dose of 50 gm/L of calcium hypochlorite *(Contact period 12 hours), removal efficiency of COD and TDS were achieved 85% and 53% respectively. Significant reduction in colour was also observed i.e. 97.5% transmittance. The residual COD i.e. 900 mg/L is thus confirming to influent standards of C.E.T.P., hence, dose of 50 mg/L was considered as an optimum dose. Figure 6 and 7 shows the variation of residual COD and TDS with different dose of calcium hypochlorite.

Probable reason for removal of COD and colour, could be the chemical oxidation of organic matter present in the wastewater.
Figure 2: Variation of residual COD with dose of different coagulants

Figure 3: Variation of residual TDS with dose of different coagulants

Figure 4: Effect of pH on TDS removal for different coagulants at respective optimum dose
Figure 5: Effect of pH on COD removal for different coagulants at respective optimum dose

Figure 6: Effect of Post Oxidation by Calcium Hypochlorite on COD Removal

Figure 7: Effect of post oxidation by calcium hypo chloride on TDS removal

Conclusion

The present studies were undertaken to characterize the wastewater generated from a typical dye intermediate industry along with the treatability studies of wastewater.
Studies were performed on laboratory scale in batch reactors to explore possible, economical viable treatment of this wastewater generated from industry. The investigative studies lead to the following conclusions.

Characteristics of wastewater from industry indicate high COD 22000 mg/l dark colour (0.5% transmittance), pH (1.36). It is observed that these parameters have values more than permissible limits of disposal to environment; therefore, it warrants treatment before disposal.

High initial COD wastewater is contributed due to organic matter viz. napthol which is used as basic raw material in manufacturing process. The napthol is an unsaturated aromatic hydrocarbon compound.

The investigatory studies lead to the following conclusions.

- The wastewater varies highly in characters.
- Characteristics of wastewater from industry indicate high COD 22000 mg/l dark colour (0.5% transmittance), pH (1.36).
- It is observed that these parameters have values more than permissible limits of disposal to environment: therefore, it warrants treatment before disposal.
- High initial COD wastewater is contributed due to organic matter viz. napthol which is used as basic raw material in manufacturing process.
- The napthol is an unsaturated aromatic hydrocarbon compound.

Among the coagulant study viz. alum, ferrous sulphate and ferric chloride, it is found that ferric chloride is a most effective one to reduce overall COD upto about 83%.

The chemically treated wastewater when further treated with calcium hypochlorite yielded in overall removal of about 97.5% and overall removal of TDS of about 63%.

The recurring cost of chemicals required for chemical treatment and post oxidation works out to be Rs. 3220/m3 wastewater. The treated effluent thus confirms the influent standards of C.E.T.P. in respect of pH, COD and colour; however, standard for TDS could not be achieved.

References


