

Decolorization and COD Reduction Efficiency of Magnesium over Iron based Salt for the Treatment of Textile Wastewater Containing Diazo and Anthraquinone Dyes

Akshaya Kumar Verma, Puspendu Bhunia* and Rajesh Roshan Dash

Abstract—Magnesium chloride, though cost wise roughly same as of ferrous sulphate, is less commonly used coagulant in comparison to the ferrous sulphate for the treatment of wastewater. The present study was conducted to investigate the comparative effectiveness of ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) as iron based salt and magnesium chloride (MgCl_2) as magnesium based salt in terms of decolorization and chemical oxygen demand (COD) reduction efficiency of textile wastewater. The coagulants were evaluated for synthetic textile wastewater containing two diazo dyes namely Reactive Black 5 (RB5) and Congo Red (CR) and one anthraquinone dye as Disperse Blue 3 (DB3), in seven possible equi-ratio combinations. Other chemical constituents that are normally released from different textile processing units were also added to replicate a practical scenario. From this study, MgCl_2 /Lime was found to be a superior coagulant system as compared to $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /Lime, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /NaOH and MgCl_2 /NaOH.

Keywords—Coagulation, Color removal, Magnesium chloride, Textile wastewater

I. INTRODUCTION

TEXTILE industry is one of the leading contributors to many Asian economies including India, as it contributes nearly fourteen percent of the total industrial production. It is also one of the biggest consumers of potable water as well as the chemical additives during various steps of textile processing. The unused chemical additives are discharged as effluent from various units in the form of wastewater. Dyeing and finishing stages are the major producer of wastewater with complex characteristics such as strong color due to the presence of residual dyes, high pH, large amount of suspended solids (SS) and high chemical oxygen demand (COD). Presence of very low concentrations of these dyes can be highly visible and hence, the receiving water bodies not only become aesthetically unacceptable but also the discharge of these effluents can be carcinogenic, mutagenic and generally very harmful to the environment [1]-[3]. Therefore, textile wastewater should effectively be treated to meet the legal as well as the aesthetic standards before discharging it into the environment or municipal wastewater treatment plant.

The conventional textile wastewater treatment technologies are normally biological, physicochemical and/or advanced oxidation processes. Biological processes are generally cheap, simple and environmental friendly, which can be used effectively to remove the biodegradable

organics but to a very lesser extent for removal of color due to less biodegradable nature of the textile dyes. Almost all advanced oxidation processes are associated with high cost of operation and may produce the toxic by-products. The main advantage of conventional physicochemical processes like chemical coagulation and flocculation, is the decolorization of wastewater takes place by removal of dye molecule from the textile wastewater, and not by the partial decomposition of dyes, which can lead to an even more potentially harmful and toxic aromatic compound [4], which can be resistant to degradation even under aerobic conditions [5], [6]. Sludge production is a major limitation associated with the chemical treatment. However, feasibility of sludge disposal makes it one of the most appropriate technology for the treatment of textile effluents.

A number of studies had been carried out for the treatment of textile wastewater containing a single dye or mixture of dyes of the same class with only distilled water for the preparation of synthetic textile wastewater [7]-[9]. Very limited studies have been reported on chemical treatment of synthetic textile wastewater containing majority of the chemical additives that are used in textile industry during different steps of textile processing. To the best of our knowledge, no study has been observed in the literature on the treatment of textile wastewater containing diverse toxic chemicals that are released from textile industries along with the mixture of widely used diazo and anthraquinone dyes. Also, very limited reported data are available on the effectiveness of iron and magnesium based coagulants along with the lime as coagulant aid on the quantity and nature of sludge production [10]. Therefore, the present study was focused to investigate the effectiveness of MgCl_2 as well as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as coagulants and lime as coagulant aid for the decolorization and COD reduction of synthetic textile wastewater containing new generation diazo and anthraquinone dyes such as Reactive Black 5, Congo Red and Disperse Blue 3 respectively, along with the various other chemical additives that are used in the textile industry during textile processing. The study was focused at evaluating comparative effect of pH and coagulant dosage for color removal efficiency along with the amount of sludge production for each of the combinations when optimum pH adjustment was carried out either by sodium hydroxide or by lime.

II. MATERIALS AND METHODS

Extra pure magnesium chloride (MgCl_2) and ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were used as coagulants and purified lime was used as coagulant aid and to increase the pH. 1.0 M H_2SO_4 and NaOH were also used to adjust the

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desired pH. The other chemical additives (namely starch, acetic acid and sucrose as sizing agents, sodium hydroxide as hydrolysing agent, sodium carbonate and sodium chloride as fixing agents, sodium lauryl sulphate as scouring agent and sulphuric acid for pH neutralization) used in the preparation of the synthetic wastewater (Table I) were of analytical grade. Dyes were procured from Sigma-Aldrich, Germany.

TABLE I
CHEMICAL CONSTITUENTS USED FOR THE PREPARATION OF SYNTHETIC TEXTILE WASTEWATER

Materials used	Concentration (mg/L)	Function
Starch	1000	Sizing agent
Acetic acid	200	Sizing agent
Sucrose	600	Sizing agent
Dyes	200	Coloring agent
NaOH	500	Hydrolysis
H ₂ SO ₄	300	pH neutralization
Na ₂ CO ₃	500	Fixing agent
NaCl	3000	Fixing agent
Sodium lauryl sulphate	100	Scouring agent

Synthetic textile wastewater was prepared as per the reported chemical constituents of real textile wastewater [11]-[13], with a total dye concentration of 200 mg/L (Table 1). The total dye concentration was prepared either with a single dye, or two and three mixed dye solutions in the equal ratio along with the various chemical additives. Wastewaters were prepared using three commercial dyes: Reactive Black 5 (RB5), Congo Red (CR) and Disperse Blue 3 (DB3) in the tap water. The maximum absorbance wavelength (λ_{max}) for each dye wastewater was used to measure the absorbance of respective treated wastewater. Color content of the wastewater containing a mixture of dyes in different combinations, was determined by taking sum of the absorbencies measured at 591, 502 and 638 nm for that particular combination [14]. The characteristics of the synthetic textile wastewater were: COD = 1980±20 mg/L, pH = 10.5±0.2, Abs(1731) = Abs(591) + Abs(502) + Abs(638) = 2.3992 for wastewater containing RB5, CR, and DB3; Abs(1093) = Abs(591) + Abs(502) = 2.4971 for wastewater containing RB5 and CR; Abs(1140) = Abs(502) + Abs(638) = 0.7638 for wastewater containing CR and DB3; Abs(1229) = Abs(591) + Abs(638) = 2.4231 for wastewater containing RB5 and DB3; Abs(591) = 3.1154 for wastewater containing RB5; Abs(502) = 0.9264 for wastewater containing CR; Abs(638) = 0.3540 for wastewater containing DB3.

The optimum pH and optimum coagulant dosage required for efficient color removal were determined by performing Jar test. Beakers of volume 1 L, containing 500 mL of wastewater were used for the coagulation experiments. Coagulant was added and mixed for 3 min under rapid mixing at 80 rpm. The solution was then mixed at slow flocculation for 15 min at 30 rpm. After sedimentation for 20 min, supernatants from the top of the beaker were taken for the analysis. Color of the samples was determined by absorbance measurement using UV-VIS Spectrophotometer

(Perkin-Elmeyer, Lambda 25). An aliquot of filtrate was then centrifuged at 7000 rpm for 10 min to obtain a clear solution. The pH of the liquid was then adjusted to about neutral for measuring the absorbance of the liquid. The COD was analysed as per closed reflux colorimetric method after digestion of the filtrates in COD reactor (Model DRB 200, HACH, USA) and then absorbance measurement was carried out by COD spectrophotometer at 600 nm (Model DR 2800, HACH, USA). COD standard curve was developed based on the absorbencies. The normalised equation $COD (mg/L) = 2500 * Abs - 165.75$ with $R^2 = 0.9994$, was derived from COD standard calibration curve, which was further used for COD measurement. The percentage color removal and COD reduction was obtained by the following equation:

$$\text{Removal (\%)} = [(A_{ut} - A_t) \div A_{ut}] \times 100 \quad (1)$$

Where A_{ut} and A_t are the absorbencies of untreated and treated wastewater sample, respectively.

Sludge production (in terms of settled sludge volume and suspended solids) was also measured at optimized conditions for all the combinations using MgCl₂ and FeSO₄·7H₂O both. All the methods used for the analysis of wastewater characteristics and sludge production were as per Standard Methods [15] and performed at room temperature (25±5°C).

III. RESULTS AND DISCUSSION

A. Determination of optimum pH for chemical coagulation of synthetic textile wastewater

The subsequent experiments were designed to determine the optimum pH for all the combinations of synthetic textile wastewater that allowed for maximum decolorization and COD reduction. Destabilisation of all the combinations was examined at various pH conditions (6, 8, 9, 10, 11, 12, 12.5) maintaining 1000 mg/L of coagulant dose for both the coagulants. NaOH and H₂SO₄ were used to control the pH for this purpose. As pH affects the molecular structure of the dyes, which changes the absorbance of the solutions [16], hence pH of the untreated wastewater as well as treated wastewater was adjusted to neutral before measuring the absorbance for evaluating the percentage of color removal. Percentage color removal increased with the increase in pH from 6.0 to 11.0 or 6.0 to 12.0. For the combinations of textile wastewater containing i) CR, ii) DB3, and iii) CR+DB3, the optimal pH was found to be 11.0, whereas for the rest of the four combinations, it was 12.0. For all the combinations, percentage of color removal was found to be decreasing at pH greater than the optimum pH. These results are in the good agreement with the findings reported by Arslan and Balcioglu [17] and Tan et al. [18]. Treatment efficiency in terms of percentage color removal and COD reduction at optimum pH for various combinations of dye wastewater has been summarised in Table II.

TABLE II
PERCENTAGE COLOR REMOVAL AND COD REDUCTION AT OPTIMIZED PH OF
THE SYNTHETIC TEXTILE WASTEWATER

Wastewater combination	Optimum pH	% of treatment efficiency with MgCl ₂	% of treatment efficiency with FeSO ₄ .7H ₂ O
RB5	12.0	93.64 (37.24)	87.25 (53.89)
CR	11.0	79.26 (34.09)	78.89 (51.68)
DB3	11.0	95.63 (39.36)	68.67 (27.88)
RB5 + CR	12.0	82.01 (32.02)	81.52 (23.22)
CR + DB3	11.0	93.90 (30.31)	90.83 (44.79)
RB5 + DB3	12.0	93.02 (28.92)	87.16 (32.99)
RB5 + CR + DB3	12.0	93.15 (19.01)	77.20 (34.52)

Note: %COD reduction is given within the parenthesis ()

The improvement of coagulation efficiency at increasing pH can be explained by the facts that, a) metal ions are easily hydrolysed in alkaline conditions and form precipitable hydroxide; b) the aggregation of selected dyes takes place at specific alkaline pH and hence, reduction in the solubility. The structure of precipitable hydroxide provides large surface area for the adsorptive removal of aggregated chemical dyes. At pH beyond 11.0 (for three combinations) and pH 12.0 (for the rest four combinations), the results show lower removal rate. This phenomenon is probably due to the increase in the solubility of hydroxide precipitate. The highest COD reduction was also observed at optimum pH for all the combinations. This might be due to the fact that starch and sucrose, which are the major sources of COD in the textile wastewater, would have been aggregated and removed along with the chemical dyes. At optimum pH, excellent reduction in color and considerable reduction in COD was observed for the wastewater containing individual dye as well as the mixture of different dyes.

B. Determination of optimum coagulant dosage

The optimum dosage of coagulants for all the combinations was determined by varying the coagulant dosage and maintaining the optimum pH either with NaOH or with lime individually. It has already been established that the lime can be used to increase the pH as well as it can work as coagulant/coagulant aid, since it is capable of giving a certain level of color removal [19]. Therefore, the present study was also conducted to evaluate the effect of lime on the color removal and COD reduction efficiency. Coagulation experiments were carried out using MgCl₂ and FeSO₄.7H₂O either with NaOH or with lime.

Color removal as a function of coagulant dosage for all the combinations is shown in Fig. 1. It was observed in almost all the cases that percentage color removal increases with the increase in coagulant dosage. Above 99% color removal efficiency was observed at 1000 mg/L of MgCl₂ for

the wastewater containing RB5 when lime was used to maintain the optimum pH. Coagulant combinations such as FeSO₄.7H₂O/Lime and MgCl₂/NaOH were also found to be effective which gave more than 96% color removal efficiency at a coagulant dosage of 1200 mg/L. However, considerable decrease in color removal efficiency of 88.6% was observed at 1200 mg/L of FeSO₄.7H₂O dose, when NaOH was used to maintain the optimum pH (Fig. 1a).

MgCl₂ in case of textile wastewater containing CR had been observed to produce excellent color removal of above 99% at a coagulant dosage of 1300 mg/L, when optimum pH was maintained by lime. Approximately, 95% color removal efficiency was observed with FeSO₄.7H₂O as well as with MgCl₂ at a coagulant dosage of 1300 mg/L when optimum pH was maintained by NaOH. However, considerable improvement by 3% in color removal efficiency for the wastewater containing CR was observed at the same dosage of 1300 mg/L of FeSO₄.7H₂O when lime was used to maintain the optimum pH (Fig. 1b).

Significant improvement in decolorization was also observed for the wastewater containing DB3 for all the coagulant combinations but comparatively at lesser coagulant dosage of 1200 mg/L. Excellent color removal efficiency of 99.8% was observed for MgCl₂ at 1400 mg/L when lime was used to maintain the optimum pH (Fig. 1c). Adjustment of optimum pH with lime over NaOH again showed the improvement in color removal efficiency. Higher treatment efficiency for the synthetic textile wastewater containing DB3 as compared to the previous two combinations might be due to the fact that disperse dyes are less soluble as compared to the other two dyes, and hence tends to aggregate at alkaline pH very easily. This observation is in good agreement with the findings reported by Arslan and Balcioglu [17], where ferrous sulphate was used for treatment of the dye bath spent containing a mixture of disperse dyes.

Color removal above 86% and 94%, respectively was achieved at 2000 mg/L of FeSO₄.7H₂O and MgCl₂ dosage for the wastewater containing RB5 and CR together, when NaOH was used for pH adjustment. However, considerable improvement in the color removal efficiency of the order 96.5% and 98.6%, respectively had been observed at the lesser dosage of 1800 mg/L of FeSO₄.7H₂O and MgCl₂, when lime was used for attaining the optimum pH (Fig. 1d).

Excellent color removal efficiencies of 99.5% and 97.1% were obtained at 1200 mg/L of MgCl₂ and FeSO₄.7H₂O respectively, for the wastewater containing CR and DB3 together, when lime was used to maintain the optimum pH. Like all other cases, in this case also treatment efficiency in terms of color removal was significantly higher than that of the observed efficiency at the same dosage of MgCl₂ and FeSO₄.7H₂O when optimum pH was adjusted with NaOH (Fig. 1e).

More than 99% color removal efficiency was obtained for the wastewater containing RB5 and DB3 together at 1200 mg/L of MgCl₂ when lime was used to maintain the optimum pH. This observed color removal efficiency was considerably higher than the other coagulant combinations such as MgCl₂/NaOH, FeSO₄.7H₂O/NaOH and FeSO₄.7H₂O/Lime even at a very high dosage of 1800 mg/L (Fig. 1f).

Color removal efficiency of 98.3% and 97% had been achieved at 1400 mg/L of $MgCl_2$ and $FeSO_4 \cdot 7H_2O$ respectively, for the wastewater containing RB5, CR and DB3 together, and when lime was used for optimum pH adjustment. However, when NaOH was used to adjust the optimum pH, decolorization efficiency of 96.5% was observed at the same dosage of $MgCl_2$ (Fig. 1g).

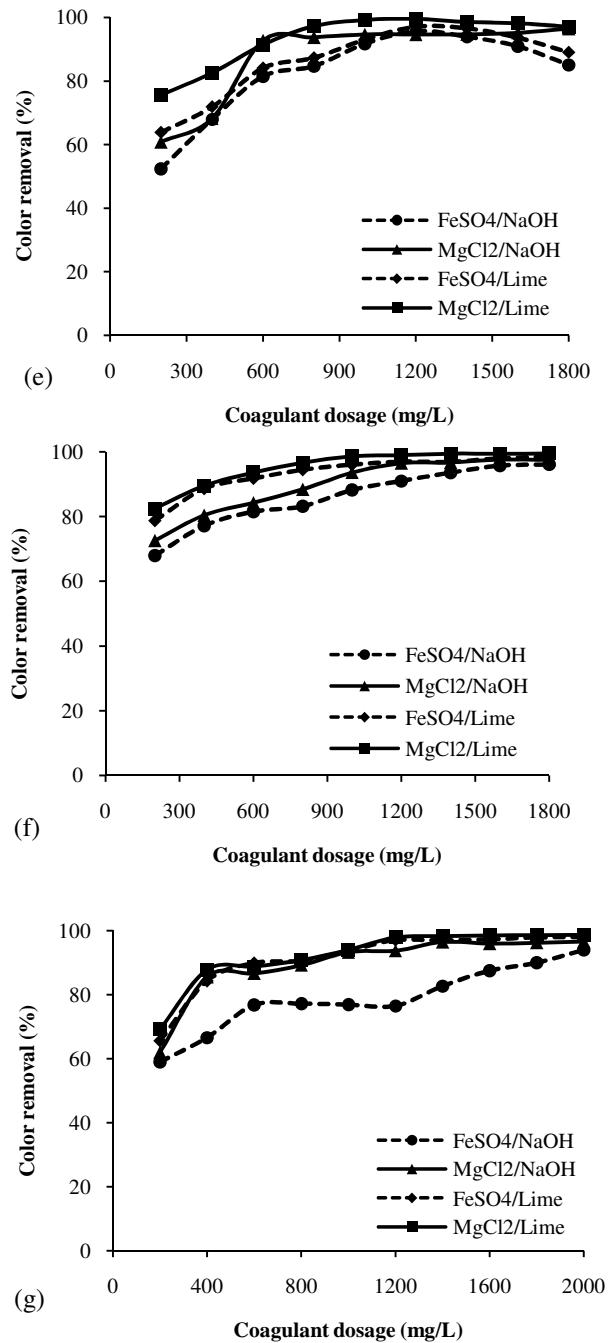
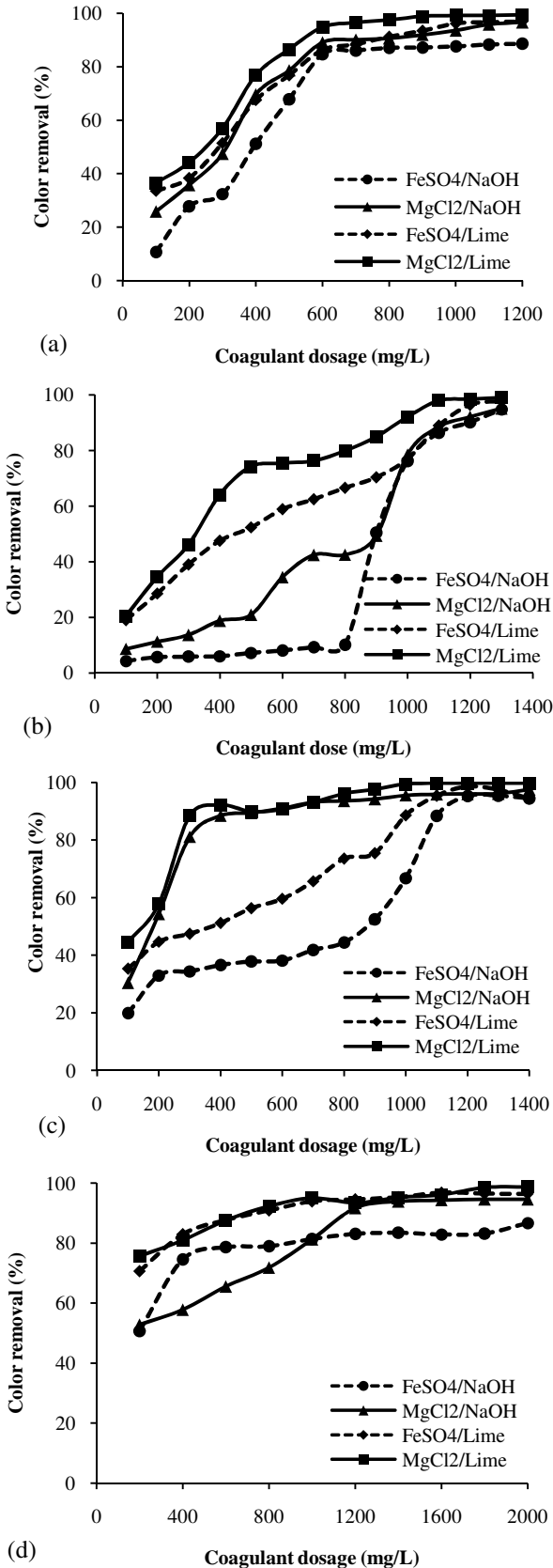
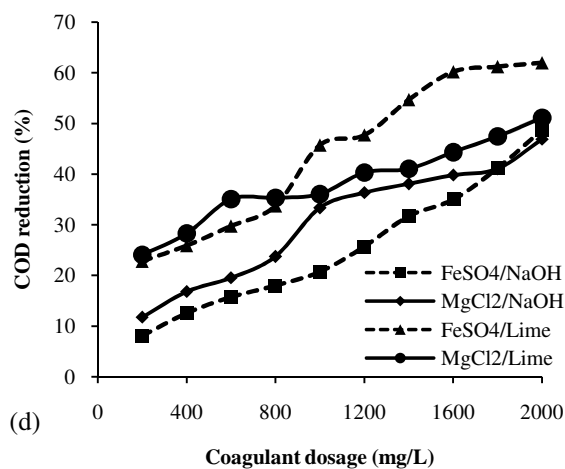
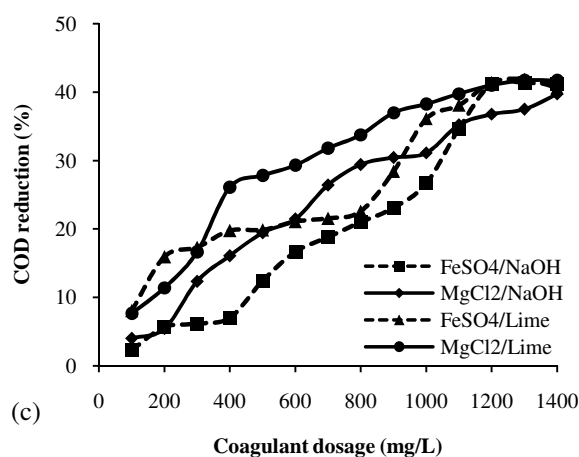
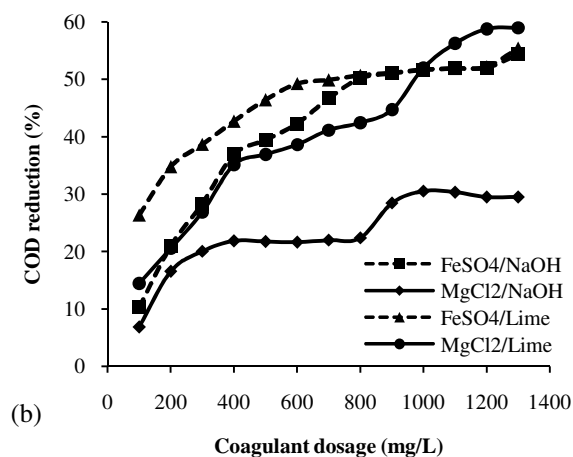
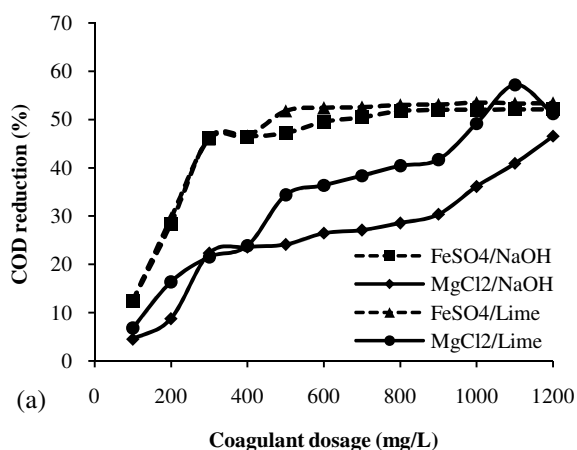


Fig. 1 Effect of coagulant dosage on the color removal for synthetic textile wastewater containing (a) RB5 (b) CR (c) DB3 (d) RB5+CR (e) CR+DB3 (f) RB5+DB3 (g) RB5+CR+DB3

Based upon the above experimental results, it can be said that DB3 (disperse dye) removal took place comparatively at the lesser dosage of coagulants as compared to the other reactive and direct dyes. This can be attributed by the fact that there might be a competitive binding of dye molecules with the coagulant according to their solubility characteristics. Faster and efficient binding upon disperse dyes may be linked to its least soluble nature. It was also observed that the synthetic textile wastewater containing CR and DB3 can be efficiently treated at a lower dosage of coagulants as compared to other combinations. Coagulation efficiency of $MgCl_2/NaOH$ was also found to be promising with observed decolorization efficiency lying between

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{NaOH}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{Lime}$ for all the combinations of synthetic textile wastewater. Further, more than 99% color removal efficiency was observed for almost all the combinations of wastewater at only 1200 mg/L of MgCl_2 with lime. Based upon the results of this study, MgCl_2 along with the lime can be proposed as the best coagulant combination for decolorizing textile wastewater.

Similar trends of COD reduction were observed with increasing coagulant dosage as obtained in case of color removal for all the combinations of synthetic textile wastewater using both $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and MgCl_2 coagulant combinations (Fig. 2). A maximum of 63.1% COD reduction was observed at the optimum coagulant dosage of 1400 mg/L MgCl_2 with lime for the wastewater containing all three dyes together (Fig. 2f). More than 50% COD reduction was obtained in case of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with lime for remaining combinations of synthetic textile wastewater as shown in Fig. 2. Comparatively, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{Lime}$ was observed as the better coagulant than $\text{MgCl}_2/\text{Lime}$ for COD reduction. This can be explained by the fact that the precipitation of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at very alkaline condition forms insoluble Fe(III) hydroxide flocs. These flocs are instrumental in leading to sweep coagulation mechanism in the presence of $\text{Ca}(\text{OH})_2$ and thereby results in better COD reduction than that of other coagulation mechanisms such as charge neutralization and adsorption, which is normally a governing coagulation/flocculation mechanism in case of MgCl_2 . Further, COD reduction capability of $\text{MgCl}_2/\text{Lime}$ was found to be lying in between $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{Lime}$ and $\text{MgCl}_2/\text{NaOH}$ for all the combinations of textile wastewater except the synthetic textile wastewater containing all three dyes together.



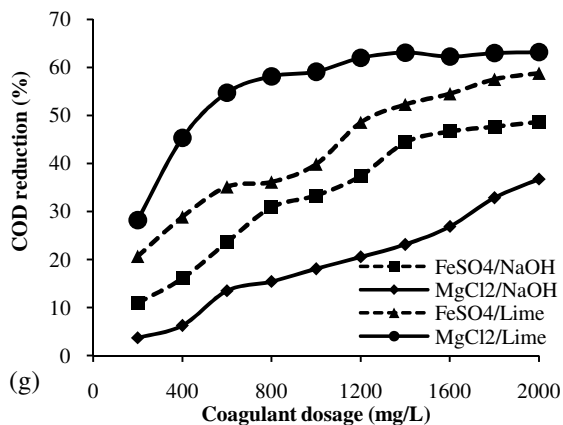
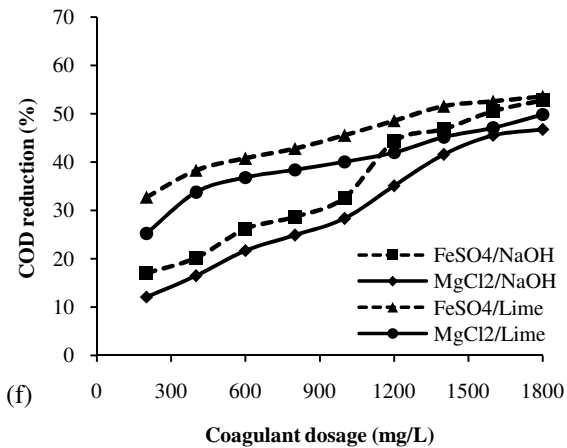
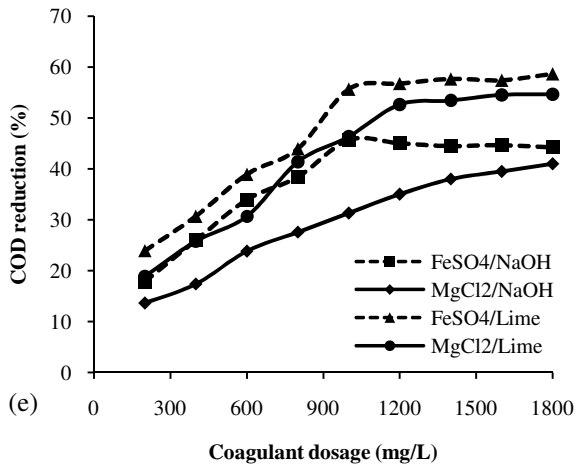


Fig. 2 Effect of coagulant dosage on the COD reduction for synthetic textile wastewater containing (a) RB5 (b) CR (c) DB3 (d) RB5+CR (e) CR+DB3 (f) RB5+DB3 (g) RB5+CR+DB3

C. Effects of lime dosage on color and COD reduction

As it was observed in almost all the above experiments that the color removal efficiency improves when lime was used either with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or with MgCl_2 for adjusting the optimum pHs instead of NaOH, hence, it indicates that lime alone as coagulant/coagulant aid can give a certain degree of color as well as COD reduction for treatment of textile wastewater. Therefore, treatment efficiency of lime alone as a coagulant was investigated for all the above combinations. For all the combinations, 800 mg/L lime dosage was found to be sufficient to attain the optimum pH, which produced 22.3% – 58.6% color removal and 17.8% – 53.5% COD reduction for different combinations of wastewater used in this study. The results of the present

study are in good agreement with the findings reported by Georgiou et al. [20], who studied the effect of lime on the color and COD reduction of real textile wastewater. However, considering the very high quantity and volume of sludge generation and very low degree of decolorization efficiency than that of the appreciable range, lime as a coagulant alone cannot be recommended for decolorization of textile wastewater.

D. Sludge production

The amount and characteristics of the sludge produced during coagulation/ flocculation depends upon the type of coagulant used and the operating conditions [21]. Therefore, sludge production was measured at optimized pH and at optimum coagulant dosage for all the combinations. It was measured based upon the volume occupied by the flocs in 500 mL of sample volume after settling for 1h in the Imhoff cone as well as the suspended solids concentration after separation of flocs from the treated wastewater with the help of filtration and the subsequent drying at 105°C for 1h. For almost all the combinations, volume of sludge produced was comparatively less when NaOH was used for pH adjustment with both the coagulants (Fig. 3). The maximum sludge production of 110 mL settled sludge/500 mL and 50 mL settled sludge/500 mL of sample were observed in case of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{NaOH}$ and $\text{MgCl}_2/\text{NaOH}$ respectively, for the wastewater containing RB5 and DB3 together. However, a maximum of 120 mL settled sludge/500 mL and 56 mL settled sludge/500 mL were observed in case of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{Lime}$ and $\text{MgCl}_2/\text{Lime}$ for the wastewater containing CR and RB5, respectively. Marginally higher sludge production when lime was used as pH adjuster can be attributed by the fact that the lime is sparingly soluble in water and therefore, it introduced suspended solids when used as coagulant aid. Further, it can also be noticed from the Fig. 3, that the sludge production was significantly less when MgCl_2 was used as the coagulant. Maximum 50 mL settled sludge/500 mL and 56 mL settled sludge/500 mL of sample were observed for the wastewater containing RB5 when pH was adjusted with NaOH and lime, respectively. Significantly reduced sludge production using MgCl_2 as a coagulant may be explained by the fact that it shows very high adsorption for the dyes and other chemical additives and produces more compact sludge as compare to the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Only 25 mL settled sludge/500 mL and 35 mL settled sludge/500 mL of sample were observed for the wastewater containing CR when pH was adjusted with NaOH and lime, respectively. This might be due to the better adsorption of direct dyes on the magnesium hydroxide precipitates as compare to the other types of dyes.

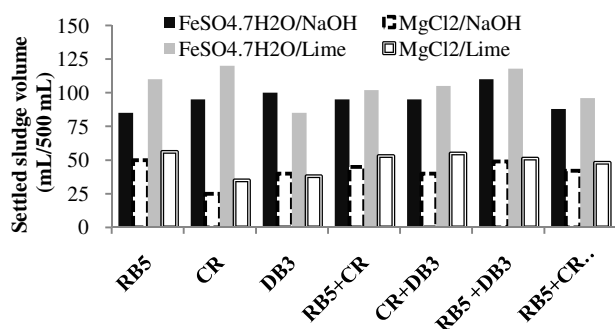


Fig. 3 Sludge production at optimized conditions for various combinations of synthetic textile wastewater

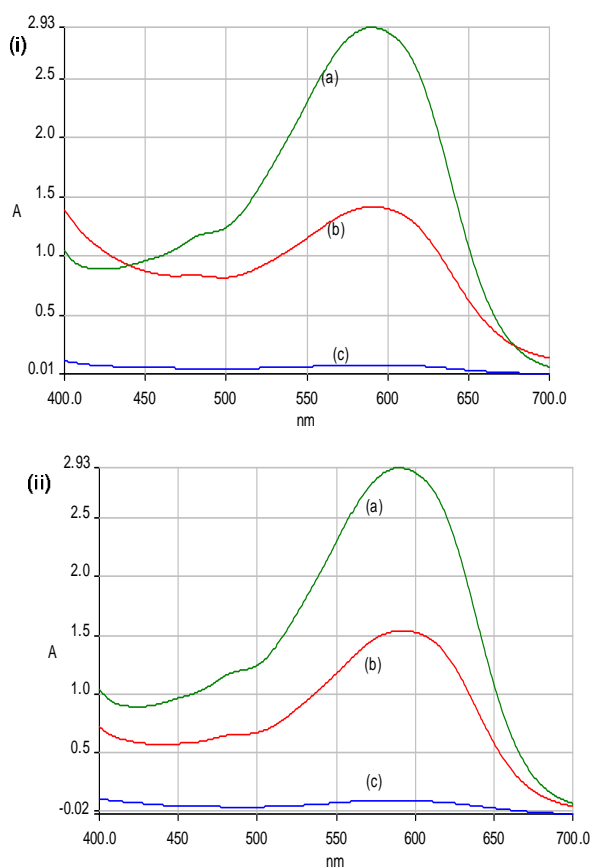
Almost reverse trend was observed during measurement of suspended solids in the case where $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was used as a coagulant. The maximum suspended solids of 1928 mg/L and 4019 mg/L were observed for the wastewater containing RB5 in case of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{NaOH}$ and $\text{MgCl}_2/\text{Lime}$, respectively. Minimum suspended solids of 862 mg/L and 281 mg/L were observed for the wastewater containing CR in case of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{NaOH}$ and $\text{MgCl}_2/\text{NaOH}$, respectively. This can be related with the characteristics of wastewater as well as the coagulant and can be explained as: (i) the wastewater containing RB5 and DB3 produces better quality (in terms of settleability) flocs as compared to that of the wastewater containing CR. (ii) MgCl_2 shows better surface adsorption than that of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The results of the present study are in good agreement with the findings reported by Bidhendi et al. [10].

E. Analysis of spectrogram and color removal mechanism of the coagulants

Spectral analysis and investigation of color removal mechanisms were performed for wastewater containing RB5, CR and DB3 dyes. All the three combination followed almost the same trends for all the four coagulant systems ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{NaOH}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{Lime}$, $\text{MgCl}_2/\text{NaOH}$, and $\text{MgCl}_2/\text{Lime}$). Therefore, wastewater containing RB5 against $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{Lime}$ and $\text{MgCl}_2/\text{Lime}$ were selected to explain the spectrogram and color removal mechanism. The spectral analysis was examined on untreated and treated wastewater at optimized condition of pH and coagulant dose (shown in the Fig. 1a). The results are shown as the curve "a" for untreated wastewater and "c" for treated wastewater, respectively in Fig. 4(i) and Fig. 4(ii). It was found that the wastewater after treatment did not show any distinctive dye peaks in the visible wavelength range from 400 to 700 nm in both the cases. This indicates that the dye from wastewater was transferred into the hydroxide precipitate obtained by coagulation-flocculation. Further, this precipitate was filtered and acidified to the neutral pH to convert into the solution. The filtrate is then analysed by spectrophotometer, and the results are shown as the curve "b" in Fig. 4(i) and Fig. 4(ii). It can be seen that the shapes of curve "a" and "b" appear to be almost similar and also the peaks have been observed to form at the same wavelength for both the cases.

The color of neutralised solution was same as the untreated wastewater but absorbance value was less. This might be due to the fact that the complete conversion of the precipitate into the solution by acidification upto neutral pH is almost impossible. Hence, it can be said that the removal

of color by coagulation was merely a physical phenomenon. There was no chemical change of dye molecules before, and after the coagulation as both the peaks have been found at the same wavelength for "a" and "b". The analysis is in good agreement with the observation reported by Gao et al. [19].



(a): Untreated wastewater, (b): After sludge digestion and neutralization, (c): Treated wastewater

Fig. 4 The spectrogram of RB5 then treated at optimized conditions using (i) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{Lime}$ and (ii) $\text{MgCl}_2/\text{Lime}$

On the basis of the findings of this study, color removal mechanisms of ferrous sulphate and magnesium chloride can be described as: (i) the metal ions from the coagulants get converted into their insoluble metal hydroxides at pH greater than 11.0, (ii) these complex and insoluble structures of hydroxides provide a large adsorptive surface area and positive superficial charge leading to adsorption and charge neutralization, (iii) finally, due to the presence of bicarbonate ions, lime reacts to form calcium carbonate precipitates, which remove dyes through the sweeping flocs mechanism [22]. Therefore, it can be said that the removal of color using ferrous sulphate and magnesium chloride as coagulant and lime as coagulant aid takes place predominantly by adsorption and charge neutralization along with the sweep flocculation principle.

IV. CONCLUSIONS

It can be inferred that the decolorization and COD reduction efficiency of coagulants significantly depends upon the pH of wastewater. Magnesium based salt appeared to be the efficient coagulant over iron based salt. Further, MgCl_2 in combination with lime was proven to be superior over the other coagulants for decolorization and COD reduction of textile wastewater. In the present study, a

maximum of more than 99% decolorization efficiency and 63% COD reduction efficiency was observed for treating synthetic textile wastewaters containing a total 200 mg/L of selected diazo and anthraquinone dyes along with other chemical additives by using $MgCl_2$ /Lime as coagulants. Reduced sludge production and excellent color removal makes $MgCl_2$ /Lime a novel and attractive coagulant system, especially for the textile wastewater having high original pH. Hence, $MgCl_2$ /Lime may be recommended as an efficient coagulant system for the treatment of textile wastewater, which removes dyes by the dual mechanisms of adsorption and charge neutralization along with the sweep flocculation. Since, this system can reduce a maximum COD of approximately 60%, the remaining COD will be more than that of the safe discharge standards set by the Environmental Pollution Authority of different countries. Therefore, the secondary treatment is required to take care of the rest of the organic matters to meet the safe discharge standards.

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