CHEMICAL ENGINEERING TRANSACTIONS

VOL. 42, 2014

A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Neven Duić

ISBN 978-88-95608-33-4; **ISSN** 2283-9216

DOI: 10.3303/CET1442030

Reclamation of Wastewater Using Composite Coagulants: a Sustainable Solution to the Textile Industries

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The present study was aimed to investigate the effectiveness of a composite coagulant {magnesium chloride (MC) added with aluminum chlorohydrate (ACH)} for the treatment of simulated as well as real textile wastewater. Simulated textile wastewater was prepared using three different categories of dyes namely, Reactive Black 5 (RB5), Congo Red (CR) and Disperse Blue 3 (DB3) in the tap water along with other chemical additives. The optimum pH for the composite coagulant was 12 at which 90 % decolourisation efficiency was obtained when both the coagulants were used in equal ratio with a combined dosage of 800 mg L^{-1}. Out of the three different coagulant dosing methods, namely, MC+ACH, ACH+MC and MC-ACH, MC+ACH at the ratio of 1.5:1 with a combined dosage of 800 mg L^{-1} was found to be the best combination, at which almost complete colour removal was achieved. The effectiveness of the composite coagulant was also verified with real textile wastewater. For real textile wastewater, 95 % decolourisation efficiency was obtained at just 1000 mg L^{-1} of combined MC+ACH (1.5:1) dosage. Adsorption and charge-neutralisation along with sweep-flocculation were proposed as the predominant colour removal mechanisms.

1. Introduction

The rapid increase of textile industries to meet the global textile demand has degraded our environment in various ways. Textile industries use huge volume of water and varieties of complex chemicals during various step of textile processing, and therefore considered as one of the most chemically intensive industries on earth and a major polluter of potable water. The unused materials from each steps are discharged as wastewater which possess strong colour due to the presence of residual dyes, high biological oxygen demand (BOD), chemical oxygen demand (COD), turbidity, pH and toxic chemicals. 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 detrimental to our environment (Šíma and Hasal, 2013). Direct discharge of these wastewaters into the open land or into the water bodies affect their ecosystem. Their presence also disturbs the aquatic life by obstructing the light penetration and oxygen transfer (Zuorro et al., 2013). Hence, to protect the water environment, textile wastewater must be treated up to the safe discharge limits as recommended by USEPA. Reclamation methods in terms of decolourisation mainly involve physicochemical, chemical and biological processes, as well as some of new emerging techniques like sonochemical or advanced oxidation processes. Each of them has some limitations and drawbacks in their application. Hence, there is no single economically and technically viable method to solve this problem and usually two or three methods have to be combined in order to achieve adequate level of colour removal. Among the currently used chemical treatment processes, coagulation/flocculation has received considerable attention because of high colour removal efficiency and ease of operation. Therefore, it can be used as a primary treatment for removal of colour prior to the biological treatment (APHA, 2005) for removal of organic matters. Regardless of the generation of considerable amount of sludge, this process is still used in developed and in developing countries. The main advantage of coagulation/flocculation method is that the decolourisation of textile wastewater can be achieved through the removal of dye molecule present in the wastewater, and not by partial decomposition of dyes, which

Please cite this article as: Verma A.K., Bhunia P., Dash R.R., 2014, Reclamation of wastewater using composite coagulants: a sustainable solution to the textile industries, Chemical Engineering Transactions, 42, 175-180 DOI:10.3303/CET1442030

could produce potentially harmful and toxic aromatic compounds (Golob et al., 2005). Also this process consumes less electrical energy as compared to the other advanced technology, thereby making the process economical for developing countries like India.

Large number of studies is available in the literature on the effectiveness of various chemical coagulants for decolourisation of textile wastewater containing single dye or a mixture of same class of dyes. Moreover, only distilled water was used to prepare the dye solution. However, very limited studies are available on the chemical treatment of synthetic textile wastewater containing majority of chemical additives that are used in textile industries during various steps of textile processing. In this continuation, Verma et al. (2012a) reported the effectiveness and superiority of magnesium based chemical coagulant over iron based chemical coagulants for treatment of textile wastewater containing various classes of dyes. Further, effectiveness of a novel aluminium based coagulants as aluminium chlorohydrate has also been report for decolourisation of silk dye bath effluents (Verma et al., 2012b). Since the dosages of magnesium chloride was higher to achieve the desired (>98 %) colour removal, therefore it was planned to use the composite coagulant for decolourisation of synthetic wastewater containing various classes of textile dye such as reactive black 5, disperse blue 3 and congo red along with the other chemical constituents that are normally during textile processing.

Therefore, the present study was focused to investigate the effectiveness of composite coagulant (magnesium chloride added with aluminium chlorohydrate) for treatment of the textile wastewater containing different classes of dyes along with the other chemical additives. The study was focused at evaluating comparative effect of pH, coagulant dosage and the dosing method on decolourisation efficiency along with the amount of sludge production when optimum pH adjustment was carried out by lime.

2. Materials and Methods

2.1 Chemicals and Textile wastewater

Extra pure magnesium chloride (MC) and industrial grade (with purity 30 % w/w) aluminium chlorohydrate (ACH) were used as coagulants. 1.0 M H_2SO_4 and NaOH were used to adjust the desired pH. Lime was also used to adjust the optimum pH, since it is well established that lime can be used as coagulant aid as well as to adjust the desired pH (Gao et al., 2007). The other chemical additives used in the preparation of the synthetic wastewater were of analytical grade.

Synthetic textile wastewater was prepared as per the reported chemical constituents of real textile wastewater (Daneshvar et al., 2006), with a total dye concentration of 200 mg L^{-1}. Wastewaters were prepared using three commercial dyes namely, Reactive Black 5 (RB5), Congo Red (CR) and Disperse Blue 3 (DB3) in the tap water along with other chemical additives. Dyes were procured from Sigma-Aldrich, Germany. The characteristics wavelength of simulated dye wastewater was determined by running a scan of the dye solution on a UV-VIS spectrophotometer. The maximum absorbance wavelength (λmax) for RB5, CR and DB3 as 591, 502 and 638 nm respectively, which were used to measure the absorbance of mixed dye wastewater. Colour content of the wastewater containing mixture of dyes was determined by taking sum of the absorbencies measured at 591, 502 and 638 nm (Wang et al., 2007). The characteristics of synthetic textile wastewater were: COD = 1,944 to 2,007 mg L^{-1}, pH = 10.4 to 10.6, Abs (mixture) = Abs(591) + Abs(502) + Abs(638) = 2.3992.

Real textile effluents were obtained from a local textile mill situated in Khurda district of Odisha, India. Similarly, the maximum absorbance wavelength (λmax) for real textile wastewater was determined as 512 nm, which was used to measure absorbance of wastewater. The Major characteristics of the effluents were: COD = 2,017 to 2,027 mg L^{-1}, pH= 8.2 to 8.5. Abs(512) = 0.5502.

The percentage decolourisation efficiency was determined using the Eq (1):

$$\text{Decolourisation efficiency (\%)} = [(A_b - A_t)/A_b] \times 100 \qquad (1)$$

where A_b and A_t are the absorbancies of the solution before treatment and after treatment of the textile wastewater, respectively. Tap water served as a reference.

2.2 Coagulation and flocculation test procedures

The optimum pH value and coagulant dosage required for efficient colour removal were determined by a jar test procedure. 1 L beakers, containing 500 mL of wastewater were used for the coagulation experiments. 1.0 M NaOH or 1.0 M H_2SO_4 was added to each beaker for pH adjustment. Chemical coagulant was added and mixed for 3 min under rapid mixing condition at 80 rpm. The solution was 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. Sludge production (in terms of settled sludge volume) was also measured at optimised conditions. All the methods used for the analysis of wastewater characteristics were as per Standard Methods (APHA, 2005) and performed at room temperature (25±3 ˚C).

3. Results and discussion

3.1 Determination of optimum pH for chemical coagulation of synthetic textile wastewater

To determine the optimum pH, a series of experiments were performed using magnesium chloride, ACH and the composite coagulant using equal ratio of magnesium chloride and ACH. The experiments were carried out at constant dosage of 1,000 mg L^{-1}, 500 mg L^{-1} and 800 mg L^{-1} respectively for MC, ACH and composite coagulant {MC+ ACH} (1:1) while varying the pH of textile wastewater from 4 to 12.5. As pH affects the molecular structure of the dyes, which changes the absorbance of the solutions (Gao et al., 1999), hence pH of the untreated wastewater as well as treated wastewater were adjusted to neutral before measuring the absorbance. The effect of pH on the colour removal efficiency at the fixed dosage of coagulants has been shown in Figure 1. Colour removal efficiency increased with increase in the pH from 4 to 12 in case of MC. Marginal reduction in colour removal was observed at pH 12.5. Therefore the optimum pH for MC can be considered as 12, at which 94 % colour removal efficiency was obtained. No continuous increasing or decreasing trend in colour removal was observed when 500 mg L^{-1} ACH was used as coagulant. However, maximum decolourisation efficiency of 55.22 % was obtained at pH 8, therefore pH 8 can be considered as optimum pH for ACH. Composite coagulant MCACH (800 mg L^{-1}) was observed to produce a maximum colour removal of 90.35 % at pH 12. This can also be observed from Figure 1, that two optimal points respectively at pH 8 and pH 12 were appeared during determination of colour removal efficiency. This confirms that the composite coagulant MCACH still posses the coagulating properties of both MC and ACH. Earlier study performed by the same authors revealed that MC is more promising for the reduction of COD as compared to ACH. While determining the optimum pH of MC, ACH and MCACH, the COD reduction of the order 59, 45 and 50 % were observed respectively.

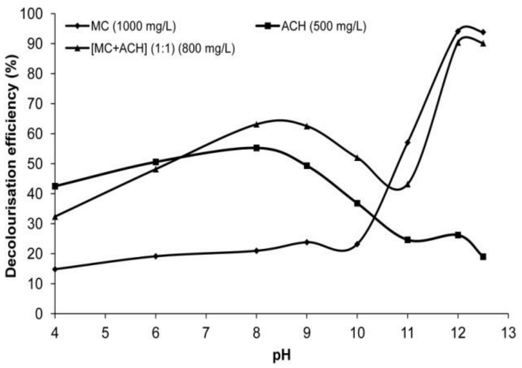

Figure 1: Effect of pH on decolourisation efficiency different coagulant combinations

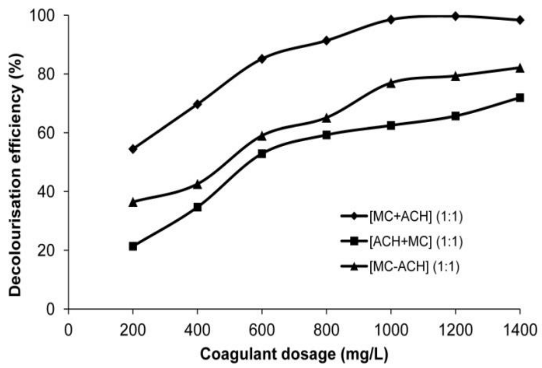

Figure 2: Effect of dosing method on coagulation of performance of textile wastewater

3.2 Effect of dosing method on treatment efficiency of textile wastewater

The studies performed by Wei et al. (2009) revealed that dosing technique of composite coagulant significantly influence the coagulation performance. This may be due to the diverse coagulating properties of the coagulants utilised for the preparation of composite coagulant. Therefore the effect of dosing method of composite coagulant MCACH was investigated for treatment of textile wastewater with three different categories as MC+ACH, ACH+MC and MC-ACH at the optimised pH of 12. Where MC+ACH denotes that MC was added prior to the addition of ACH in the textile wastewater. Similarly, ACH+MC indicates that MC was added after the addition of ACH and finally MC-ACH signifies that pre-mixed composite coagulant was added for the coagulation of textile wastewater. From the Figure 2, it can be observed that colour removal efficiency continuously increases with increasing concentration of composite coagulants. Highest colour removal efficiency over 99 % was obtained using MC+ACH at an equal ratio combined dose of 1,200 mg L^{-1}. ACH+MC and MC-ACH were observed to produce 72 and 82 % decolourisation efficiency, respectively at an equal ratio combined dose of 1,400 mg L^{-1}. The significant variation in the coagulation performance using different dosing techniques can be related with the optimum pHs for both the coagulants as well as the ability to remove the different dye types. MC effectively decolourise textile wastewater containing almost all the types of textile dyes including reactive dyes at higher pH, whereas ACH was found to be promising for the decolourisation of textile wastewater containing disperse and acid dyes including silk dye wastewater (Verma et al., 2012a). The combined coagulants MC+ACH interact with the textile wastewater as follows: i) pre-addition of MC at its optimum pH effectively removes reactive dye present in the textile wastewater with the mechanism of adsorption and charge neutralisation and simultaneously reduce the pH of wastewater, ii) reduced pH favours the coagulation performance of ACH, thus post-addition of ACH to the wastewater now effectively removes the residual dyes present in the wastewater with sweep flocculation mechanism.

Addition of ACH prior to MC at pH 12 was not suitable since the optimum pH of ACH is around 8 and therefore poor decolourisation efficiency had been observed in case of ACH+MC. Similarly, optimum pH conditions for pre-mixed coagulant were also not suitable for the effective coagulation and results in reduced decolourisation efficiency. Like decolourisation efficiency, COD reduction efficiency also depends upon the coagulation performance of different coagulants and the highest COD reduction efficiency of 52 % was obtained with MC+ACH at a dose of 1,200 mg L^{-1}.

3.3 Determination of optimum coagulant dosage for chemical coagulation of textile wastewater

The optimum dosage of coagulants for efficient chemical coagulation of textile wastewater was determined by varying the coagulant dosage and maintaining the optimum pH with lime. 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 because of its potential to give a certain degree of colour removal (Verma et al., 2012a). The effect of coagulant dosage on decolourisation efficiency was investigated using MC, ACH, MC+ACH (1:1) and MC+ACH (1.5:1). During experiment, it was observed higher dosage of composite coagulant was required to produce the virtually colourless treated effluent when MC in equal ratio with ACH was used as coagulant. In previous study by the authors, it was observed that MC is highly effective in removing reactive dyes compared to ACH even at higher coagulant dosage. Therefore, it was planned to increase the concentration of MC in the composite coagulant which may decrease the combined dosage of composite coagulant effectively by precipitating the reactive dye present in the wastewater.

Decolourisation efficiency as a function of coagulant dosage for the different coagulant combinations is shown in Figure 3. Decolourisation efficiency of more than 99 % was observed at 1,600 mg L^{-1} of MC as a coagulant. ACH was also observed to give promising decolourisation efficiency of 97.23 %, but at very higher dosage of 2,000 mg L^{-1}. The higher dosage requirement using ACH may be related to the poor adsorption of reactive dyes onto the ACH flocs. Use of composite coagulant in equal ratio produced considerable improvement in decolourisation efficiency over the case when MC or ACH was used alone as coagulant. MC+ACH (1:1) gave excellent decolourisation efficiency of 99.66 % at the reduced combined coagulant dosage of 1,200 mg L^{-1}. It was observed during experimentation that increased ratio of MC in composite coagulant may further decrease the combined coagulant dosage since the treated solution was containing only reactive residual dye. Therefore, MC+ACH (1.5:1) was used as composite coagulant to decolourise the textile wastewater. Further improvement in the decolourisation efficiency was observed even at all the coagulant dosage. MC+ACH (1.5:1) produced highest colour removal of 99.91 % at a combined coagulant dosage of 1400 mg L^{-1} which was marginally higher to the colour removal produced by MC+ACH (1:1). Additionally, the excellent colour removal of close to 99 % was observed just at 800 mg L^{-1} combined dosage, which was far superior over the colour removal produced by MC+ACH (1:1) at same dosage.

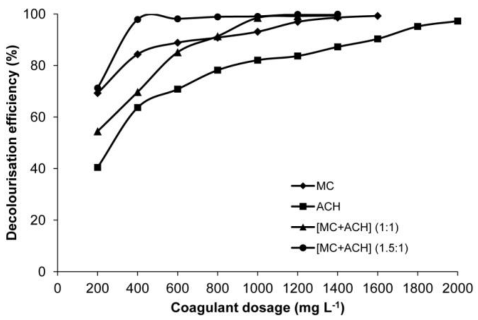

Figure 3: Effect of coagulant dosage on two different ratios for decolourisation

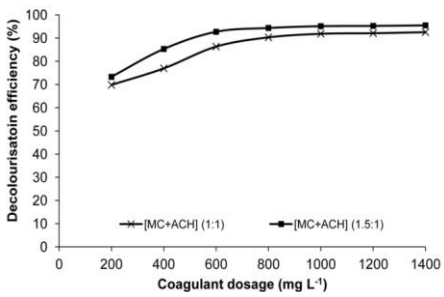

Figure 4: Effectiveness of composite coagulant at decolourisation efficiency of textile of wastewater real silk dyeing wastewater

3.4 Effectiveness of composite coagulant for the treatment of real silk dyeing

To verify the effectiveness of composite coagulant for the treatment of real silk dyeing wastewater, a similar test procedure as of the synthetic textile wastewaters has been carried out. The decolourisation efficiency of real silk dyeing wastewater was carried out at its original pH (8.2~8.5), just to assess the sustainability of the composite coagulant at two different ratios of MC+ACH. Distinctive variation in the decolourisation efficiency was observed with two different ratios of MC+ACH at all the dosage. Highest decolourisation efficiency of 95.46 % was observed with MC+ACH at 1.5:1 ratio, which was significantly higher than the decolourisation efficiency (92.55 %) achieved at 1:1 ratio. Close to 95 % decolourisation efficiency was also achieved at significantly lesser dosage of 1000 mg L^{-1} MC+ACH with ratio of 1.5:1 (Figure 4). The observed findings clearly reveal the effectiveness of increased proportion of MC for decolourisation of real textile wastewater. In addition to this, experimental results show the suitability of the composite coagulant for decolourisation of wide variety of textile wastewater.

From this study, it can be said that the MC+ACH is not only an efficient composite coagulant for the decolourisation of synthetic textile wastewaters but also for real textile effluents. The higher dosage requirements for decolourising real textile wastewater compared to synthetic textile wastewater can be linked to the difference in residual dyes concentration as well as the type of dyes being used and complexity of wastewater. The observed optimum dosage of composite coagulant was considerably lower than that of the dosage required for other metallic coagulants reported by the several other researchers for the treatment of textile wastewaters (Patel and Vashi, 2010). Thus, MC+ACH as a composite coagulant can be considered as one of the most efficient and sustainable solution for the reclamation of textile wastewaters.

3.5 Sludge production

The quantity and quality of the sludge produced during coagulation/flocculation depend upon the type of coagulant used and the operating conditions (Amuda and Amoo, 2007). Therefore sludge production, in terms of settled sludge volume was measured at optimised pHs and at optimum coagulant dosage for synthetic and real textile wastewater using different coagulant combinations. The settled sludge volume was measured based upon the volume occupied by the flocs in 500 mL of sample volume after settling for 1h in the Imhoff cone.

It can be observed from the Figure 5 that a maximum of 95, 100, 97, and 96 mL settled sludge per 500 mL of sample was produced respectively with MC, ACH, MC+ACH (1:1) and MC+ACH (1.5:1) at the optimised conditions. 100 mL settled sludge per 500 mL of real silk dyeing wastewater was observed when treated with MC+ACH (1.5:1) (Figure 5). Slightly higher volume of sludge production as compared to the case of synthetic textile wastewater may be attributed to the more complex nature of real silk dyeing wastewater and fragile flocs formation during coagulation. Significantly higher volume of sludge production has been reported by Bidhendi et al. (2007), who investigated the sludge production during treatment of industrial dyeing wastewater using alum, $FeSO_4$, $FeCl_3$ and $MgCl_2$ at their optimised pH. Treatment efficiency of a coagulant is strongly related to the type of hydroxides formed and their solubility. ACH generally forms $Al(OH)_3$, $Al(OH)_2^{+}$ and $Al(OH)^{2+}$ including the dominant polymeric species as Al_{13}^{7+}, during hydrolysis at lower pH (Wang et al., 2008), which remove dyes through adsorption and charge-neutralisation.

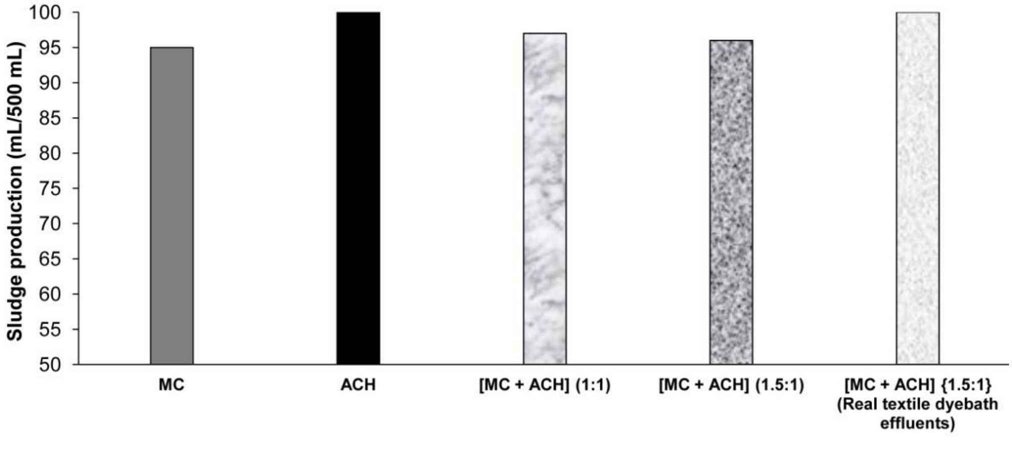

Figure 5: Sludge production at optimised conditions for synthetic and real textile wastewater using different coagulant combinations

Further, the hydrolysis of MC at higher alkaline pH in aqueous phase forms complex insoluble hydroxide flocs, which provide large adsorptive surface area and high positive superficial charges and hence leading to the adsorption and charge-neutralisation. In addition to this, in the presence of bicarbonate ions, lime reacts to form calcium carbonate precipitates, which removes dyes by enmeshing them into the formed precipitates and thereby removes through the sweeping flocs mechanism (Semerjian and Ayoub, 2004). Therefore, it can be said that removal of colour using MC+ACH as composite coagulant and lime as coagulant aid takes place predominantly by adsorption and charge neutralisation along with the sweep flocculation mechanism.

The reclaimed water thus obtained, posses high alkaline pH, which can effectively be used at the dyeing and printing stages. Deep dyeing and printing stages generally require the high alkaline environment to favour its fixation onto the fibres. The reusability of the treated textile wastewater makes the process attractive and sustainable to the textile industries.

4. Conclusions

As MC was demonstrated to be very effective for the decolourisation of wastewater containing reactive dyes, whereas ACH possess ability to removes other types of dyes effectively. Therefore decolourisation of textile wastewater using MC+ACH was very much effective because of its dual advantage having both the characteristics of aluminium and magnesium salts. The highest decolourisation efficiency of close to 99 % and 95 % respectively, were observed for synthetic and real textile wastewater in this study with the composite coagulant as MC+ACH (1.5:1). Reduced and easily dewaterable sludge production, and excellent treatment efficiency even at lesser dosage of composite coagulant makes MC+ACH a novel coagulant combination and may be recommended for industrial application. The treated effluent quality satisfies the requirements of water quality for dyeing and finishing process mainly for deep coloration. Therefore, textile wastewater reclamation and reuse is a promising alternative associated with the present technique, which can both conserve and reduce or eliminate the global environmental pollution due to the textile industries.

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