Treatment of tannery wastewater using aluminium formate: influence of the formate over sulphate-based coagulant

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Abstract

Tannery industries provoke the conspicuous quantity of deleterious effluent which has to be treated prior to discharge into the environment. Pre-treatment of tannery wastewater with aluminium sulphate is well known over decades, but due to the corrosive nature of sulphate this pre-treated water causes several issues in the biological treatment system. To overcome this issue a study was performed to understand the coagulant activity of aluminium formate and aluminium sulphate. The effect of coagulant activity as a function of pH and coagulant dose of Aluminium formate was studied and found that it surpassed aluminium sulphate in terms of Cr(VI), sulphate and COD removal by 10%, 6% and 10% respectively, while turbidity removal for both coagulants was found approximately equal. Possible mechanistic approach to the coagulation property of aluminium formate and aluminium sulphate could be inter particle bridging and sweep coagulation respectively. Formate [$HCOO^-$] can be utilized as a counter anion in the place of commonly used sulphate anions as it is biodegradable, non-toxic and corrosive free compound. Therefore, Aluminium formate can be a promising coagulant for the pre-treatment of tannery wastewater.

Keywords: Tannery wastewater, coagulation, Aluminium formate, Hexavalent chromium, Formate ion.

Abbreviations: AF, Aluminium formate; AS, Aluminium sulphate; COD, Chemical Oxygen demand; UV, Ultraviolet; BOD, Biochemical Oxygen demand; Cr(VI), Hexavalent Chromium; [$HCOO^-$], Formate ion.

1. Introduction

Although leather industry is presently undergoing a drastic conversion due to increasing pollution and discharge legislations (Deghles and Kurt, 2016); however, in developing countries like Turkey, China, India, Pakistan, Brazil and Ethiopia (Lefebevre *et al.*, 2006; Banu and Kalippan, 2007), tanneries represent the prodigious economic input. Among them, the Indian leather industry is 6th largest in the world and it is one of the top ten foreign exchange earners for the country. More than three thousand tanneries are present in India and around 80%

are under small scale sector (Sharma and Adholeya, 2011) but regrettably it is an important source of pollution. Tanneries necessitate a series of chemical treatments and mechanical operations to accomplish the require traits (Elabbas *et al.*, 2016). During the chrome tanning process, Cr(VI) is used for tanning that ingest 30-35L of water per kg of skin. However, 40% of Cr(VI) salts are frequently remitted into the final effluents which causes a serious threat to the environment and distress to the internal organs as well as external organs of the human body such as kidney, liver, respiratory tract , skin etc., it also deforms the DNA, which leads to the genetic transformation (Barrera-Diaz *et al.*, 2012; Dalcin *et al.*, 2011). In addition, it provokes 90% of used water as effluent which comprise high amount organic matter, suspended solids, BOD, Cr(VI), COD and Sulphate (Aboulhassan *et al.*, 2008). The pollutants with high concentration as well as low biodegradability represent an increasing environmental alarm with regard to environmental challenge (Schrank *et al.*, 2009).

The treatment of tannery wastewater is more complicated due to the accumulation of complex organic and inorganic compounds. Many researchers have reported the Pre-treatment technologies of tannery wastewater; some of the methods like i.e., flotation, electrochemical treatment, sedimentation, coagulation, filtration, ultra-filtration, reverse osmosis process (Song *et al.*, 2008). Coagulation or chemical precipitation has been known for wastewater treatment over centuries, where lime was used as coagulant alone and/or in combination with cationic or anionic polymers which increases treatment efficiency. In addition, the pH and coagulant dose plays a vital role as it helps in the agglomeration of slow-settling micro-flocs into larger-denser flocs (Radio *et al.*, 2004; Liu *et al.*, 2012). Among these pre-treatment methods, coagulation/flocculation process is one of the most simple, efficient and considered technique to improve the biodegradability and fouling of tannery wastewater. In addition, it is suitable to enhance the effectiveness of subsequent treatment and to provide low cost and efficient biological treatment (Shammas, 2005). Depending on the contaminant and the type of coagulant in pre-treatment process with high efficiencies, it removes COD, turbidity,

sulphate and heavy metals (Maranon *et al.*, 2008). Aluminium sulphate [$Al_2(SO_4)_3$] and ferric chloride [$FeCl_3$] salts are commonly used coagulants to treat tannery wastewater. Aluminium sulphate has advantages over Ferric salts in many ways as it is comparatively better in case of the degree of interaction between aluminium cations, the target principal contaminant Cr(VI) and its easy availability as well as cost-effectiveness (Mella *et al.*, 2015). The drawbacks of using ferric salts in tannery wastewater treatment are during unharing process, it produces dark black color due to the formation of Iron sulfide (Sayers and Langlais, 1977). Some researchers had found that due to the usage of coagulants aluminium and ferric salts in huge dose leads to the residual metal in treated water as well as sludge produced by metal salts is normally porous, incompact and difficult to dewater as it has high moisture contents of 99–99.7% (Zhao and Bache, 2002). In tannery wastewater, chloride and sulphates are one of the major problems in biological treatments due to the high concentration of Chloride which retards biodegradation of dissolved organics and sulphate also causes corrosiveness to various materials during pre-treatment of coagulation process (Maharaja *et al.*, 2017; Mikola and Tanskanen, 2015). In order to overcome these problems, it is necessary to find an alternate coagulant to treat the wastewater with no toxic effects.

The objective of the present study is to evaluate coagulant activity of Formate [$HCOO^-$], which can be used as a counter anion by substituting commonly used sulphate and chloride anions in aluminium coagulants. The reason to consider coagulant is that, it is less corrosive than chloride and sulphate and can be decomposed easily and agglomeration of anions in treated water can be eluded (Vaananen *et al.*, 2012; Talu and Diyamandoglu, 2004). Biodegradability empowers the processed water to be used in irrigation without causing salinization of the soil and also the other prospective of the formate anion can be used to aggrandize the performance of biological process which follows coagulation as a pre-treatment (Mikola and Tanskanen, 2015).

In the present study, the effect of operational conditions was examined and optimization of coagulant behaviour was scrutinized, on the basis of the coagulant activity for removal of Cr(VI) and also elaborated the other factors such as COD, turbidity and sulphate. The possible mechanism of aluminium formate coagulant was also compared with that of traditional aluminium sulphate coagulant with the help of SEM analysis.

2. Materials and methods

2.1. Chemicals and reagents

2.1.1. Chemicals for Physico-chemical analysis

1,5-Diphenylcarbazide ($C_{13}H_{14}ON_4$), Sodium Acetate ($C_2H_3NaO.3H_2O$), Potassium Nitrate (KNO_3), Ferrous Ammonium Sulphate Hexahydrate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$), were procured from Loba Chemie, India, Acetone (CH_3COCH_3), Nitric acid (HNO_3), Magnesium chloride Hexahydrate ($MgCl_2.6H_2O$), Acetic acid (CH_3COOH), Barium

chloride ($BaCl_2.2H_2O$), Ammonium chloride (NH_4Cl), Aluminium sulphate [$Al_2(SO_4)_3$], Sodium chloride (NaCl), Sodium hydroxide (NaOH), Ferroin indicator solution were purchased from Merck, India. Silver Sulphate purified (Ag_2SO_4) was brought from Central Drug House (P) LTD, India.

2.1.2 Reagents used for synthetic tannery waste water

Potassium dichromate ($K_2Cr_2O_7$), Kaolin, Humic acid, Barium Sulphate ($BaSO_4$), Calcium chloride ($CaCl_2.2H_2O$), were purchased from Merck, India. Dipotassium hydrogen orthophosphate ($K_2HPO_4.3H_2O$) was supplied by Fisher Scientific, India. Aluminium Hydroxide $Al(OH)_3$ was provided by S.d. Fine-Chem (P) LTD, India and Formic Acid was brought from Sisco Research Laboratories (P) LTD, India. All the reagents were prepared in Millipore water (Merck, Germany).

2.1.3. Preparation of synthetic tannery wastewater

Synthetic tannery wastewater was prepared in laboratory conditions by simulating real tannery wastewater whose selected constituents were of Potassium dichromate ($K_2Cr_2O_7$) 100 mg/L was added in order to improve the Cr(VI) concentration in the solution. In addition, Humic acid powder was added as organic matter to make it as a real tannery waste water, whose required concentration and pH were prepared for optimization study in bench scale coagulation experiments.

2.2. Synthesis of Aluminium formate

Aluminium formate was synthesized by adding 3:1 ratio of Formic Acid and Aluminium Hydroxide as starting materials. The solution was heated carefully on a hot plate at a temperature of 45 °C. As a result, a strong robust reaction takes place and the temperature was slightly increased to 90° C the solution was turned into solid form and dried in oven at 105° C for 20 (Mikola and Tanskanen, 2015). The formed solid was grinded using blender to convert into fine powder form.

2.3 Preparation of metallic coagulant solution

The coagulant solution of Aluminium formate [$C_3H_3AlO_6$] was prepared by dissolving 2.5 g in 250 ml of distilled water. While the solution of aluminium sulphate [$Al_2(SO_4)_3$] was prepared in the same separately. The solutions were mixed vigorously to get the homogenized solution of the respective coagulant.

2.4 Optimization experiment

Synthetic tannery wastewater was carried out using a jar test method (Scientific Engineering Corp., India) the pre-determined pH was adjusted using 1N H_2SO_4 /1N NaOH, where the contents were continuously stirred, followed by the coagulant dose of aluminium formate and aluminium sulphate separately. The pH and dose of the coagulant varied from 6.0-8.5 and 50-450 mg/l respectively. During the bench scale coagulation experiments, to control the unwanted dilution effects coagulant volume was maintained less than 5% v/v (aqueous solution basis) (Khayet *et al.*, 2011). After the dose of coagulant, the

paddle was rotated at a speed of 400 rpm for 1 min and followed by a slow mixing of 20rpm for 15 min then the water was allowed to settle for 30min to achieve floc growth (Vaananen *et al.*, 2012) and Cr(VI) was measured using a UV Spectrophotometer for pH and dose optimization.

2.5 Analytical methods

The analysis of coagulant treated wastewater for various parameters like pH, turbidity, conductivity, Cr(VI), COD and sulphate were measured as per prescribed method i.e. (APHA, 2012). The turbidity and pH were measured using a Digital turbidity meter (E. I, India) and bench scale pH meter (Hanna Instruments, Germany) respectively. Whereas Cr(VI) and Sulphate were measured using UV–Vis spectrophotometer (UV-Vis spectrophotometer, Labtech Model No. 91008) at 540 nm and 420 nm respectively using quartz cell as prescribed method i.e., (APHA 2012). Cr(VI) was measured by taking 5ml of sample in a beaker and pH was adjusted to 1.0 by using 0.2 N HNO_3 and then the sample was make up to 100 ml using the distilled water. 2ml of DCP (1,5-Diphenylcarbazide ($C_{13}H_{14}ON_4$)) solution which was prepared by dissolving 250 mg in 50 ml of acetone was added and left to stand for 5 minutes to develop pink colour and the readings were taken by using the spectrophotometer immediately. Sulphate measurement was carried out by taking 100ml of filtered sample in a beaker in which 20ml of freshly prepared buffer solution was added as the method reported by

(APHA, 2012) and a pinch of Barium chloride ($BaCl_2.2H_2O$), was added to form a white precipitate and the readings were taken at 420 nm using spectrophotometer. COD was measured by a close reflux method using COD digester (HI 839800 Hanna Instruments, Germany) and morphological study were carried out using an SEM analyser (Zeisis, Germany). All experiments were conducted in triplicates for reproducibility purpose.

2.6 Morphological characteristics of coagulants (SEM analysis)

The morphological characteristics of the agglomerates of aluminium formate and aluminium sulphate were examined by using scanning electron micrographs. Fig. 1(a) depicts the presence of small globular structure on the surface of aluminium formate, which corresponds to an occurrence of the interparticle bridging phenomenon among flocs. In Fig. 1(b), flocs of bigger size were observed, which reveals honeycomb structure of agglomeration and it elicits the possibility of adsorbed colloidal particles inside the porous structure of aluminium sulphate. Though aluminium formate might not be as efficient as aluminium sulphate in floc formation, but it poses the ability to adhere small flocs together by this we can conclude that interparticle bridging and sweep flocculation could be the possible mechanistic approach for aluminium formate and aluminium sulphate coagulants respectively (Miller *et al.*, 2008).
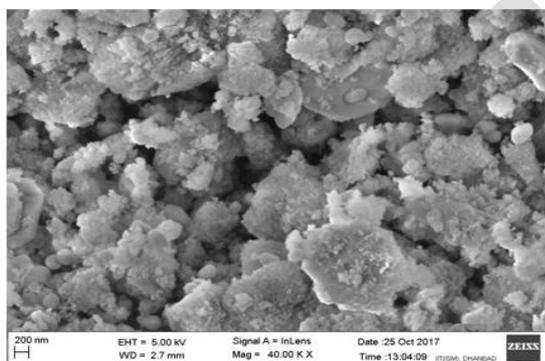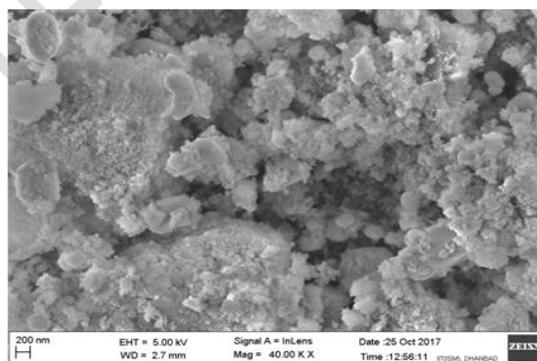
(a)   (b)

Figure 1. (a) and (b) depicts the FE-SEM analysis of aluminium formate and aluminium sulphate

3.   Results and discussion

3.1. Characteristics of raw tannery wastewater

To evaluate the coagulant activity of two aluminium species coagulants namely aluminium formate and sulphate, the real tannery wastewater samples were collected from the leather complex of Calcutta and the concentration of different pollutants was monitored. Based on the physico-chemical analysis and different literatures on actual tannery wastewater, the synthetic tannery wastewater was prepared.

Table 1 represents the concentration of different physico-chemical characteristics of real and synthetic tannery wastewater.

To understand the coagulant activity of aluminium formate Cr(VI), sulphate, turbidity, and COD were selected as the variable parameters for the optimization study during coagulation.

3.2 Optimization study

The optimum pH and dose for coagulation was determined based on the removal efficiency of Cr(VI) reduction at various pH and coagulant dosages. The effect of pH at initial Cr(VI) concentration of 100 mg/L and dose of coagulant has been shown in Fig. 2(a) and Fig. 2(b) respectively.

Table 1. Physico-Chemical characteristics of raw and synthetic tannery wastewater

| Parameters	Actual Conc	Synthetic conc
pH	9	9.4
Conductivity (μs/cm)	12900	11860
Total dissolved solids (mg/L)	6900	5782
Sulphate (mg/L)	916	760
Chemical oxygen demand (mg/L)	17600	16000
Turbidity (NTU)	87	82
Cr(VI) (mg/L)	120	100
Chlorides (mg/L)	1200	599.8

***conc**- Concentration*

3.3 Effect of pH on Cr(VI) removal

Cr(VI) oxidation state is more lethal than Cr(III) state due to high solubility and mobility of the oxy-anion forms, which exists in two forms namely, chromate anions in acidic condition as hydrogen chromate ($HCrO_4^-$) and chromate anions (CrO_4^{2-}), which is dominant species in alkaline medium (Aroua *et al.*, 2007). The pH plays crucial role in the removal of Cr(VI) from tannery wastewater. Results showed that 70-80 % of Cr(VI) was removed in alkaline condition while lower coagulant activity was observed at acidic pH, which might be due to the occurrence of competition between protons and metal ions for common binding sites under acidic condition (Sutherland *et al.*, 1989; Song *et al.*, 2004; Chowdhury *et al.*, 2013). Fig. 2(b) depicts the influence of coagulant dose on the removal of Cr(VI) at an optimum pH 7.5, as the dose of the aluminium species coagulant increases at a rate of 50 mg/L, the removal efficiency of Cr(VI) was increased up-to optimized dose for both the coagulants.
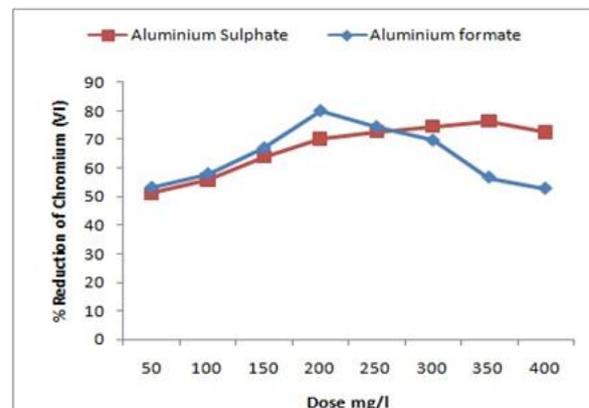
3.4 Effect of coagulant dose on Cr(VI) removal

Fig. 2(a) illustrates the increasing Cr(VI) removal efficiency of both coagulants, aluminium formate and aluminium sulphate with the increase in pH, which might be due to the generation of aluminium bridged oligomers and high polymers (as a result of hydrolysis of aluminium species). Due to these reactions, the efficiency of the coagulant was

also improved through electrostatic interactions of colloid species (Wilson, 2014). The maximum percentage removal, nearly 80% Cr(VI) was observed in case of aluminium formate; the reason might be that the aluminium formate ($C_3H_3AlO_6$), decomposes into Aluminium (Al^{+3}) and formate ions ($HCOO^-$) in the synthetic tannery wastewater. The formate ion ($HCOO^-$) further dissociates and releases CO_2 and H^+ ions. Moreover, H^+ ions react with Cr(VI) present in the synthetic tannery wastewater and thereby gets reduced to Cr(III) and these Cr(III) has a tendency to bind with OH^- ions and precipitates as Chromium hydroxide [$Cr(OH)_3$]. Fig. 2(b) shows that the removal efficiency of Cr(VI) in case of aluminium formate reduces after optimized dose i.e. 200 mg/l. The decline in removal efficiency after optimized dose was because of re-stabilization effect, as the coagulant dose surpassed the threshold level (Chowdhury *et al.*, 2013). Whereas in the case of aluminium sulphate, maximum 70% Cr(VI) removal was observed at a dose of 350 mg/l. The low removal efficiency of Cr(VI) was due to the slow hydrolysis rate of the aluminium sulphate, because the counter anion present in aluminium sulphate to some extent binds to the positive sites of the impurity particles as a result increase in the negative net charge of the pollutants. Due to this phenomenon higher dose of coagulant is needed for charge neutralization in order to precipitate out the pollutants (Saukkoriipi, 2010).
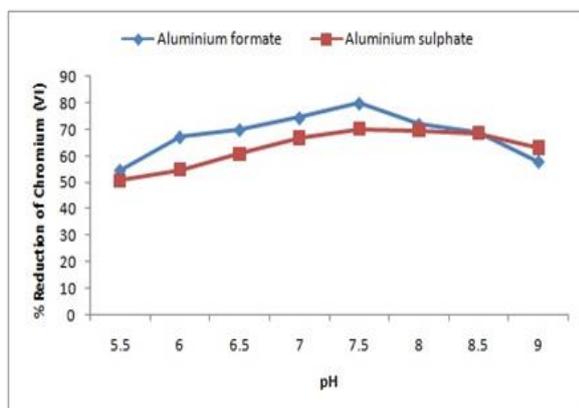

(a)

(b)

Figure 2. Effect of coagulant on Cr(VI) removal as a function of (a) pH (b) Dose

3.5 Effect of coagulants on removal of Turbidity

Turbidity is a measure of water quality and is a measurement methodology that involves light reflection which passes through water without being absorbed and scattered. In the Fig. 3, it shows that at an optimum pH both Aluminium formate and aluminium sulphate coagulants exhibited the removal efficiency of turbidity almost nearly about 90% and 94% respectively with the increase of the coagulant dose and results in a decrease of residual turbidity. It was perceived that as the dose of aluminium coagulants reached to an optimum value there was no further decrease in the residual turbidity, which signify that over dose of coagulant leads to re-stabilization of colloidal particles (Yan *et al.*, 2007). In aluminium formate (organic) coagulant size of the floc was comparatively smaller with that of aluminium sulphate. However, it showed better particle agglomeration resulting in adhesion of organic and inorganic contaminants this might be due to interparticle bridging. But in the case of aluminium sulphate at higher pH 6-8 formation of $Al(OH)_3$ was significant where at lower pH Al^{+3} were present in considerable amount which are effective in coagulation because they destabilize the negatively charged impurity particles entrapped and precipitates as flocs as a result the efficiency of turbidity was increased the possible mechanism might be sweep flocculation (Kim *et al.*, 2007).
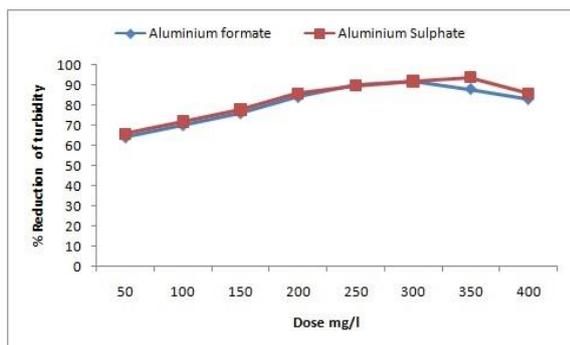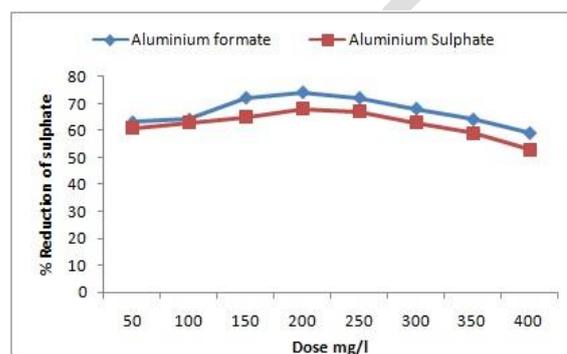

Figure 3. Effect of coagulant dose on the removal of turbidity

3.6 Effect of coagulant dose on the removal of sulphate

High concentrations of sulphate can lead to environmental problems, corrosion and scaling of equipment (Lens and Pol, 2000). In fig 4, the graph illustrates that at an optimum pH the coagulant species of aluminium format showed its maximum removal efficiency nearly about 74% at a low dose concentration, aluminium formate decomposes into aluminium and formate anions. The aluminium binds with the counter anion sulphate which is present in tannery wastewater and forms aluminium sulphate. This aluminium sulphate has the capability to generate aluminium hydroxide precipitates at neutral/ alkaline pH, which are either positively or negatively charged by the adsorption of hydroxometallic ions onto the surface. Thus, this surface charge can modify the probability for the fixation of sulphate ions conspicuously. Similar mechanism occurred for the removal of sulphate anions in the case of aluminium sulphate coagulant. The removal efficiency of aluminium

sulphate was low as compared to aluminium formate coagulant, because high dose of aluminium sulphate caused a reduction in removal efficiency due to the higher solubility of aluminium species and the increased pH. The reason might be negatively charged surface of the aluminium hydroxide precipitates associated with the adsorption of alumina hydroxo anions, which prevents the adsorption of sulphate (Canizares *et al.*, 2008; Lacasa *et al.*, 2013; Mamelkina *et al.*, 2017). Mamelkina *et al.*, (2017) also reported that, higher solubility of sulphate increases the pH level up to 12 which reduced the removal efficiency of sulphate ions significantly in the wastewater.

Figure 4. Effect of coagulant dose on reduction of sulphate

3.7 Effect of coagulant on the removal of COD

The COD removal efficiency was found about 70% using aluminium formate coagulant, while aluminium sulphate showed low percentage removal nearly about 60%. Fig 5 elucidates that at optimum pH, the removal of COD was increased with an increase in the dose of the coagulant until it reaches to the optimum value and started to retrograde.
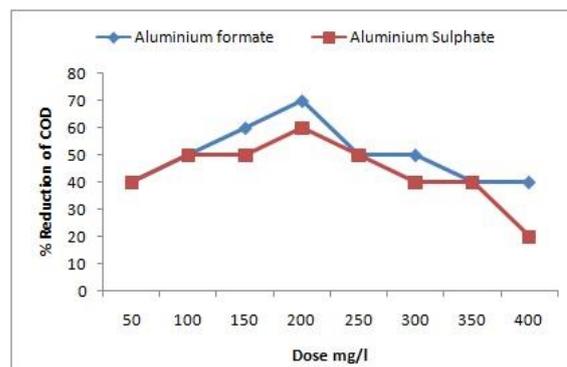
Figure 5. Effect of coagulant dose on the removal of COD

In aluminium formate, the organic and inorganic suspended contaminants adhere on the surface might be due to interparticle bridging. However, as the dose of the coagulant increases the surface charge of the particles will be reversed at higher dose due to uninterrupted adsorption of mono and polynuclear species of the coagulant. In aluminium sulphate the maximum particle removal occurred by sweep flocculation due to the

synchronized effect of charge neutralization and adsorption of aluminium ions, hydrolyzed aluminium flocs enmeshed the colloids and drown them to settle down (Verma *et al.*, 2010; Srivastava *et al.*, 2005; Garg *et al.*, 2005).

4. Conclusion

In the present study, the coagulation efficiency of aluminium formate, which was synthesized from aluminium hydroxide with the reaction of formic acid was assessed for the treatment of tannery wastewater. The effectiveness of aluminium formate over aluminium sulphate was evaluated under different operational conditions and the results were compared in terms of Cr (VI), sulphate, and COD removal efficiency. The higher Cr(VI) removal efficiency was achieved using aluminium formate over aluminium sulphate even at a low dose concentration, which might be due to the decomposition of aluminium formate, which further dissociates and releases CO_2 and H^+ ions as a result H^+ ions reacts with Cr(VI) and reduces to Cr(III), which has a tendency to bind with OH^- ions and precipitates as $Cr(OH)_3$. The high sulphate removal may be attributed as aluminium binds with sulphate which produces aluminium hydroxide precipitates at neutral/alkaline pH and acts as a primary coagulant species and reduces sulphate ions in a quick response time. Literature also suggested that Formate acts as counter anion and has more advantages over sulphates and chlorides due to its less corrosiveness and no toxic effects. Aluminium formate may acts as a carbon source from the coagulant that may be used as a nutrient in biological processes. Based on the above facts, Aluminium formate is a promising prospective coagulant that can be used in the place of aluminium sulphate for the treatment of tannery wastewater.

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