Distillery wastewater treatment by coagulation method

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Abstract: This work is an attempt to treat distillery wastewater using coagulation process where ferric chloride and aluminium chloride are used as coagulant. The maximum COD and color reduction were achieved 70% and 45% respectively with ferric chloride at their optimum condition while aluminium chloride provided maximum COD and color reduction of 62% and 39% respectively. Furthermore, ferric chloride provided better settling as compared to aluminium chloride. Results indicated that coagulation is well applicable to treat distillery wastewater.

Keywords: Distillery wastewater, COD reduction, Color reduction, Settling, Waste Minimization

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INTRODUCTION

Alcohol is important constituent for preparation of different chemical and medicine hence its demand increases day by day. Additionally, ethanol is good blending material for gasoline cause the cost of gasoline significant reduced. Around 60% ethanol is produced by sugarcane. However, sugar cane availability is once of year. Hence industries try to shifted other raw material like rice grain because its availability is throughout the year.

The production of ethanol completed in two stages including fermentation and distillation. The fermented material contains only 9-12% ethanol hence after the distillation large amount of wastewater coming out from bottom of distillation column. This waste water is called spent wash (SW) that contain very high COD and color. Hence it is first treated in biodigester where significant amount of organics is reduced. The treated water of biodigester is called biodigester effluent (BDE) that still contain very high COD. If it is directly discharge in any water source without any treatment source may being fully contaminated. Hence its further treatment is required.

Coagulation is traditional but effective method for the treatment of a various type of wastewaters. Coagulation has been mostly used to treat synthetic wastewaters and industrial wastewater to remove undesired material. The treatment of rice grain-based BDE by coagulation is one of the good choices to treat it. In recent years, several surveys of the literature on the subject indicates the attempts that have been made to find an ultimate solution to this problem.

Few works have been published to removal of organics from the BDE of rice grain-based distillery. Prajapati et al (2015) reported their work for the treatment of BDE from rice grain distillery using inorganic coagulant. Therefore, it has been felt desirable to undertake studies to improve our understanding on the use of coagulation process for wastewater treatment.

The present study has been undertaken with the following objectives:

1. Characterization of BDE from a nearby rice grain-based alcohol distillery
2. Study of the coagulation/flocculation process for the treatment of BDE and the effect of operating parameters such as the type of flocculant, pH, flocculant dosage, etc.
3. Characterization of the treated effluent after coagulation.

MATERIAL

(a) Chemicals: The BDE effluent and treated effluent are analyzed for different parameter using analytical reagent (A.R.) grade chemicals. Laboratory reagent (L.R.) grade $FeCl_3$, and

$AlCl_3$ chemicals are supplied from the Merck Ltd, Mumbai (India) to accomplish coagulation experiments. Wattman filter paper was imported from the GE Healthcare Ltd, Buckinghamshire (U.K).

(c) Waste Water Sample: The effluent was obtained from a distillery industry located at Kumhari, CG, India. The BDE sample is stored in a deep freezer at 4°C to maintain constant characteristics of BDE. The characteristics of BDE sample are given in Table 1.

Table 1. Typical composition of biodigester effluent and treated effluent

Parameters	BDE
COD	11800
TDS	45130
TSS	39312
TS	74442
Chlorine	134
Total hardness	9025
Sulfate	4920
pH	7.6
Color	Blackish brown
Absorbance at wavelength = 475nm	0.912
Color (PCU)	442

*All value in mg/dm^3 except pH and color

EXPERIMENTAL SETUP AND PROCEDURE

COAGULATION

Coagulation/flocculation studies were done in a jar. The jar test is one of the common and easy laboratory method used in coagulation/flocculation studies. Six jars (500 to 1000 ml capacity) for six different coagulation conditions are placed in a multiple stirrer. Speed controller was used to control the stirring speed. After this jar was kept constant for few hours for settlement of sludge. Finally, the supernatant liquor was filtrated by Wattman filter paper (no 42) and analyzed for its COD and color. Above method is applied for other coagulants. 0.5 dm^3 measuring cylinder is used to perform settling

ANALYSIS OF RAW EFFLUENT AND TREATED EFFLUENTS

As earlier discussed, that several compounds are presented in the biodigester effluent (BDE). The analysis for some of the components was carried out using standard methods.

Close reflux method is used for the determination of COD of the sample. The concentration of chloride is determinate by titramatric method (Vogel, 1958). Digital pH meter (EI Made, India) is used for the determination of pH of the sample. The color of the samples is measured by spectrophotometry method at absorbance of λ=475 (Migo et al., 1993; Chaudhari et al., 2007).

RESULTS & DISCUSSIONS

TREATMENT OF BIODIGESTER EFFLUENT USING INORGANIC COAGULANTS

The BDE from the rice grain based distillery have high color appearnce due to the presence of melanoidin and have very high COD. The melanoidin is refractory in nature as well not easily biodegradable. This section presents the results on the effect of two coagulants, namely $FeCl_3$ and $AlCl_3$ for the reduction of COD and color from the BDE. The characteristics of the $FeCl_3$ and $AlCl_3$ are given in Table 2. The impact of different parameter including pH_0 and the coagulant dosage on COD and color removal are also studied. For economic and operational standpoint, the settleability of the coagulated mixture have significant role. Hence settling studies are also done to know the settling characteristics. UV- spectrophotometer is used to measure, the color of the filtrate in terms of the absorbance at λ = 475 nm.

Table 2. Characteristic of $FeCl_3$ and $AlCl_3$

Characteristic	$FeCl_3$	$AlCl_3$
Appearance	Brownish yellow solid	Light yellow solid
Lead	Nil	Nil
Al/Fe/Cu content	0.348	0.204
Iron	-	0.05%
Sulfate	Nil	0.01%
pH of 1% solution	0.78	2.77

MECHANISM OF COAGULATION

The rice grain based BDE contains number of organic materials. All organics have own functional groups that passes net negative ions. Melonoidin is complex in nature and that does not have an exact formula. Possibly it can be formulated as CH_3–CO–R, which releases negative charge (Migo et al, 1997). The BDE contains large amount of colloidal particles. The colloidal surfaces have negative charge. When aluminum-based coagulant (like $AlCl_3$ alum) and iron-based coagulant (like $FeCl_3$) are dissolved in water, the metal ions hydrate and hydrolyze to form of several monomeric and polymeric species. Both Al^{3+} and Fe^{3+} presence in the BDE, and produce metal precipitates in term of $Fe(OH)_3$ or $Al(OH)_3$ as any variation in the pH or coagulant dosage (Dentel and Gossett, 1988). The general form of the hydrolysis reaction of trivalent metals is represented as (Ching et al., 1994):

$$x\,M^{3+} + y\,H_2O \;=\; M_x(OH)_y^{(3x-y)+} \;+\; y\,H^+ \qquad (1)$$

The ions of aluminium and iron are hydrated in water that leads to the formation of a primary hydration shell with six octahedrally coordinated water molecules, e.g. $Al(H_2O)_6^{3+}$ (Gregory and Duan, 2002), these ions is often shown as a successive deprotonation of water molecules in the primary hydration shell. For example, in case of Al^{3+}, successive deprotonation may lead to various aluminum hydroxide ions formation as explained in the equations below

$$Al^{3+} + H_2O \;\rightarrow\; AlOH^+ \;+\; H^+ \qquad (2)$$

$$Al^{3+} + 2H_2O \;\rightarrow\; (AlOH_2)^+ \;+ 2H \qquad (3)$$

$$7\,Al^{3+} + 17\,H_2O \;\rightarrow\; Al_7(OH)_{17}^{4+} \;+\; H^+ \qquad (4)$$

$$Al^{3+} + H_2O \;\rightarrow\; Al(OH)_3 \;+\; 3H^+ \qquad (5)$$

The hydroxide of iron and aluminium have amorphous structure, significant surface area, and offers positive charge (Randatke, 1988). Hydrophobic nature offers by these metal hydroxides that easily absorb organic particles and become insoluble (Dentel and Gossett, 1988; Ching and Tanaka, 1994). Therefore, water and slurry have different phase.

Coagulant/flocculant generate metal hydroxide (solid hydroxides) which have different solubility. Aluminum and iron produces, most stable, solid hydroxides which have gibbsite and goethite, respectively, which take months to reach equilibrium. However in coagulation/flocculation practice, amorphous precipitates plays significant role as these are formed very rapidly (Gregory and Duan, 2001). Ferric species show a much lower solubility (about 20 nM) over a broad pH range while Al species have minimum solubility (about 2 nM) at around pH 6. Other anions like fluorides, phosphate and sulfate, increases the precipitation rate of hydroxides. It may also enhance the solubility of metals at lower pH values (Gregory and Duan, 2001). The polynuclear hydrolysis product of aluminium, e.g., Al_{13} polymer, $Al_{13}O_4(OH)_{24}^{7+}$ is highly effective in neutralizing the negative charge of colloids in water.

The metal cations of iron and aluminium tend to associate and complex with different organics that contained oxygen functional groups especially with polar molecules (Ching et al., 1994). These functional groups releases local negative charge that neutralized by the positive charges of aluminium and iron, consequently the heavy flock formation along with metal (cations) – organic (anions) complexes precipitation. In this condition both organics and inorganic solids form into large, amorphous flocs due to the adsorption and bridging (Jeckel, 1986).

It is reported that (Srivastava et al., 2005) the critical concentration of the coagulant (CCC) increases with increase in valency of the cation that promotes to start hydrocolloids into coagulating and precipitating. Thus, it can be say that the CCC of $AlCl_3$ or $FeCl_3$ reaches required condition that offers Al^{3+} or Fe^{3+} cations (Chaudhari et al, 2007).

EFFECT OF PH

Coagulation/flocculation efficiency depends individual functional groups present in the organics that participated in the the coordination and complexation with metal cations at a individual pH. Generally, organics removal efficiency of from BDE during the coagulation practice with metal salts of iron and aluminium at varying pH condition offers two distinct mechanisms. In the acidic condition insoluble metal complexes formation occurs due to anionic organic molecules coordinate that present in the effluent. On the other hand with basic pH along with elevated coagulant doses, pre-formed flocs of metal hydroxides adsorb organics and get precipitated (Chaudhari et al, 2007).

The COD and color removal efficiency of treated sample (BDE) with various coagulants are given in Figure 1 and 2 respectively. The effect of coagulants with varying pH in the range of pH 3 to pH 11 was studied for both coagulants. It can be observed that COD and color removal efficiency of the BDE strongly depends on pH. Iron based ($FeCl_3$) coagulant provided maximum COD and color reduction of 70% and 45% respectively at pH 7. Additionally, COD removal efficiency decreased for pHi < 7 and pHi 7. Similar type trend obtained for coagulant $AlCl_3$ where COD and color removal efficiency increased from pH 3 to 7 and further increase in pH both COD and color removal efficiency decreased till pH 11. The maximum COD and color removal efficiency with $AlCl_3$ was observed 62% and 39% respectively.

Coagulants such as $FeCl_3$ and $AlCl_3$are acidic in nature. It reduced pH of e BDE when added in it. From the Figure 1 and Figure 2 demonstrated that individual coagulant has own optimum pH and any changes in the pH can highly affected the result of the experiment. For both coagulant the $FeCl_3$ and $AlCl_3$ the optimum pH was 7. Hence it may be concluded that the color and COD reduction of BDE highly depends on pH.

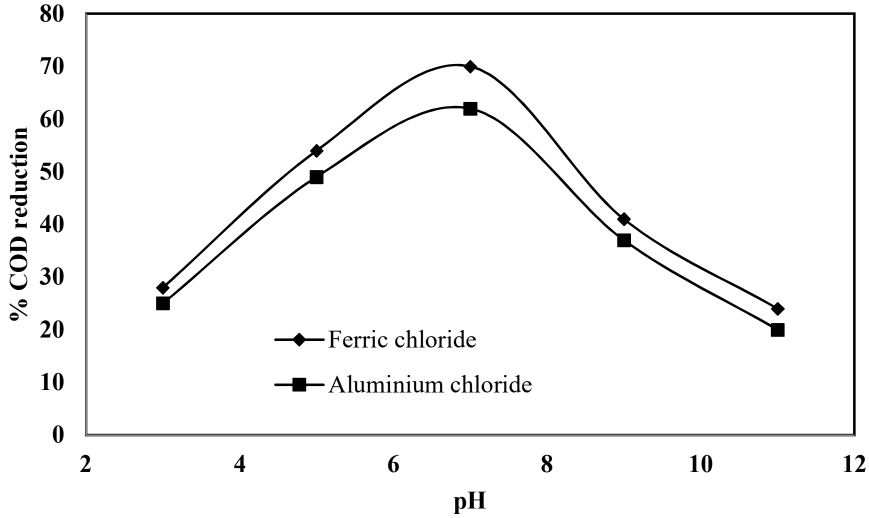

Figure 1. Effect of pH on COD reduction

The decolourization is reflected by the decrease in absorbance percent of the treated BDE sample against the original sample at λ = 475 nm (Migo et al, 1993; Chaudhari et al, 2005). During the coagulation process significant melanoidin is reduced consequently color removal efficiency increases. The amount of COD and color reduction depends on components and on the amount of metal cation, metal hydroxide and methyl hydroxide cations present in the effluent. The behaviour of functional are different with individual pH. The color reductions are found less as compared to COD reductions for all pH due to little amount of microparticle still present in treated effluent.

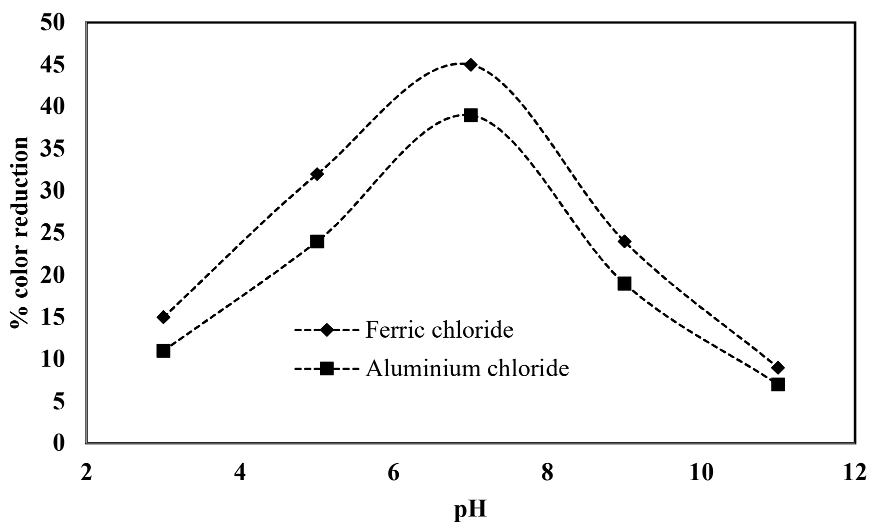

Figure 2. Effect of pH on color reduction

EFFECT OF COAGULANT DOSAGES

Number of experiments has been performed to optimize the coagulant dose of $FeCl_3$ and $AlCl_3$ based on COD and color removal efficiency of BDE. The results are presented in Figure 3. and Figure 4 Percentage COD reduction obtained with a 1 gram/dm^3 (Al^{3+}) aluminum chloride and (Fe^{3+}) ferric chloride were 45% and 37% respectively. The values have increased continuously to 70% and 62% respectively with coagulant dosages of 3 g/dm^3 metal cations. After 3 g/dm^3 coagulant dosage, the COD reduction decreases. Because overdosing of coagulant promotes restabilization of neutralized organic anions (Peavey and Rowe, 1985). Chaudhari et al (2010) reported similar type results during the treatment of pulp and paper effluent using coagulation process.

The color removal efficiency of BDE with varying mass loading of coagulants is given in Figure 4. The $FeCl_3$ showed a 45% color reduction with their optimum dosage 3 g/dm^3. Further increase or decrease in coagulant dose, the percentage color removal decreased. The maximum removal efficiency with $AlCl_3$ was achieved 39% at their optimum loading 3 g/dm^3 metal cations in their coagulant. Figure 4 reflect that color removal efficiency increases with coagulant dosages from 1 g/dm^3 to 3 g/dm^3. However, further increase in coagulant dosages color removal efficiency. Excess dosages of coagulants destabilize and neutralizes the organic anions thereby causing for higher color intensity.

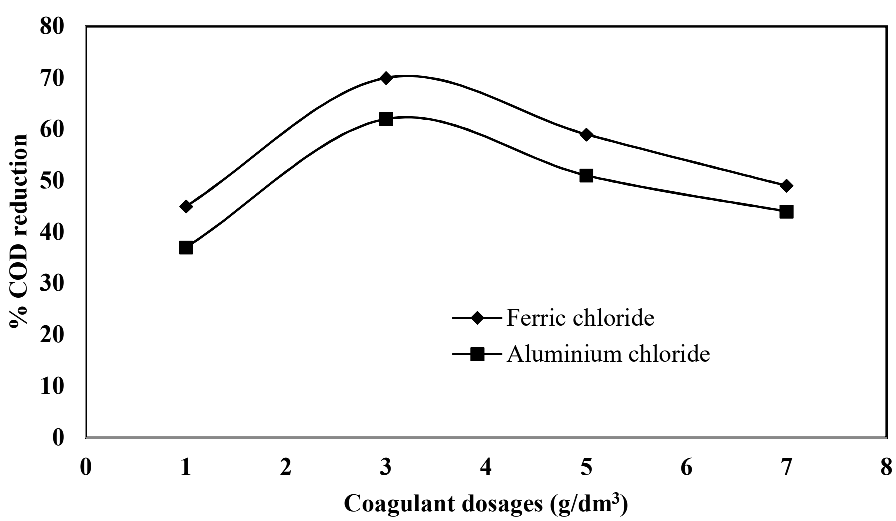

Figure 3. Effect of coagulant dose on COD reduction

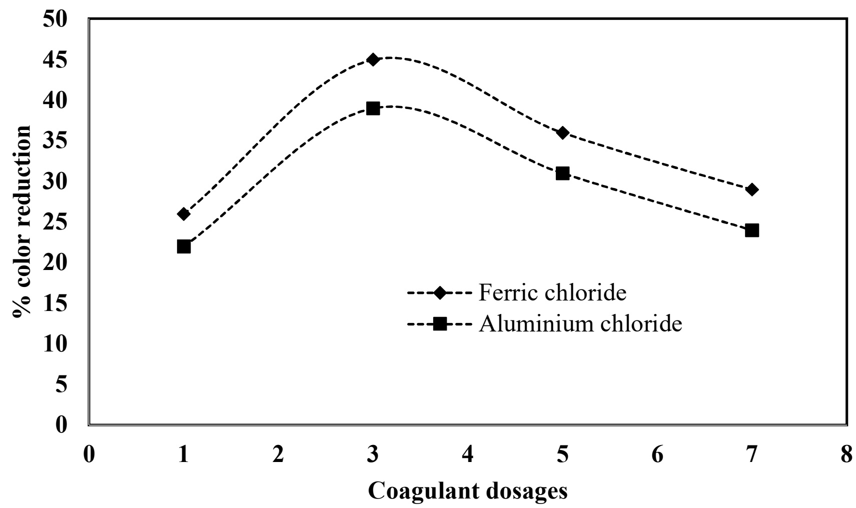

Figure 4. Effect of coagulant dose on color reduction

5.3.4. Settling Study of the Treated Effluent

Handling, treatment and disposal of the sludge generated at the wastewater treatment plants during the coagulation process has been a great challenge of its inevitability which may give rise to collateral pollution and has been one of the serious problems in the field of water pollution treatment. The determination of sludge characteristics is necessary. Chemically coagulated flock differs significantly from the flocks formed during electrocoagulation. The disadvantage of flocculated flocks over flocks generated during EC treatment is that the former contain less bound water and are more resistant to shear (Barkley et al., 1993).

To perform the settling characteristics of coagulated sludge, the treated BDE sample was well mixed and put into the 0.5 dm^3 cylinder having diameter 4.6 cm. Now the cylinder should be kept constant and measure the position of upper interface in calculated time interval. Each sedimentation test should be performed around 80-90 minutes. Settling was plotted in terms of dimensionless height of the solid-liquid interface (H/H_0) as a function of settling time. Initially the fast-settling rate was observed that decreased with respect to time. The settling rate was found in the order of $FeCl_3$ > $AlCl_3$ (Figure 5). $FeCl_3$ was provided better settling as compared to $AlCl_3$ because the formation of amorphous, gelatinous, heavy flocks, which settled by gravity. Generally, batch sedimentation data used to design a continuous thickener (Richardson et al, 2003). The method proposed by Richardson et. al. (Richardson et al, 2003) is similar to the design of a continuous thickener based on batch studies.

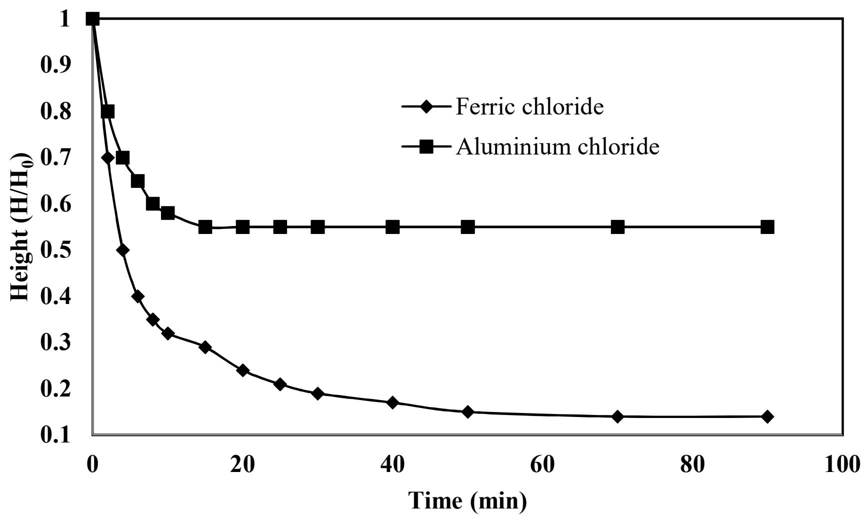

Figure 5. Settling characteristics of coagulated sludge

CONCLUSIONS

Based on the present study subjected to coagulation of BDE using $FeCl_3$ and $AlCl_3$ as inorganic coagulant the following conclusions can be drawn:

1. The BDE contain several organic and inorganic substances, which contribute to the high COD and color of the effluent.
2. It is demonstrated from the present work coagulation is very effective method to treat rice grain-based distillery BDE.
3. $FeCl_3$ provided better results as compared to $AlCl_3$
4. Maximum COD and color reduction of 70% and 39% respectively were achieved with inorganic coagulant $FeCl_3$ at pH 7 and coagulant dose of 3 g/dm^3. On the other hand, with $AlCl_3$ coagulant maximum COD removal 62% and color removal of 39% were observed at optimum condition.
5. $FeCl_3$ treated BDE provided better settling Characteristic as compared to $AlCl_3$.
6. Coagulation process did not achieve complete removal of COD and color from the BDE hence further treatment is required.

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