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Decolorization and removal of chemical oxygen demand (COD) of rice grain–based biodigester distillery effluent (BDE) using inorganic coagulants

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ABSTRACT

The removal of COD and color from biodigester effluent (BDE) of rice grain–based distillery was studied using inorganic coagulants such as $CuSO_4{\cdot}5H_2O$, Alum, $FeCl_3$, $AlCl_3$, and $FeSO_4{\cdot}7H_2O$. The $CuSO_4{\cdot}5H_2O$ was found to be the best among all coagulants provided maximum 91% COD reduction and 85% color reduction with 60 mM Cu^{2++} at a optimum initial pH (pH_i) 6. The pH of the effluent/coagulant mixture showed significant role in the removal of harmful substances from the BDE. Settling and filterability characteristics of the treated BDE slurry were found to be dependent on coagulant type and treatment conditions. High COD and color reductions of the BDE in the coagulation process show a better alternative to the conventional bio-aerobic treatment process applied for the treatment of wastewater.

Keywords: Rice grain–based biodigester effluent; Chemical oxygen demand; Settling; Filtration; Coagulation

1. Introduction

The alcohol industry is one of the largest agro–based industry. Of the total world demand of ethanol, nearly, 61% is produced from sugar cane [1]. Due to current trends of using ethanol and ethanol-blended gasoline as motor fuel, there is a gap in the demand and supply of ethanol which cannot be overcome by using common raw materials, such as sugar cane and sugar beat. Therefore, the raw materials to be used for the production of ethanol has been shifted to grains like wheat, rice, and maize. India is the largest rice-producing country in the world; therefore, Indian distilleries use nonedible grade rice as a major supplement raw material in place of sugar cane and molasses. Advantages of using rice grain to produce ethanol are its low price and generation of relatively less harmful effluent as compared to sugar cane and sugar beat–based distilleries. Now, India is producing 0.22 million m^3/year ethanol from the rice grain, which is only 10% of total alcohol production. Since sugar cane and the molasses are seasonal crops, rice grain is a good option to run the industry throughout the year.

Ethanol is produced by fermentation process that contains 5–10% (v/v) of alcohol, remaining is called spent wash (SW). The alcohol is separated in distillation

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column as a top product, and SW comes out as the bottom product. The characteristic of SW depends on raw material and the process used by the industries. SW is the primary effluent of the distillery. The rice grain–based SW contains COD (35,000–50,000) mg/dm^3 and BOD (7,000–10,000) mg/dm^3, and it is sent to the biodigester for anaerobic treatment. Treatment in a biodigester reduces 50–70% COD and 70 to 90% BOD, from the spent wash. But effluent of the biodigester (BDE) still contains high COD (10,000–14,000) mg/dm^3 and BOD (1,500–3,000) mg/dm^3. Most of distillery in the world uses an aerobic biodigestion process to treat BDE. But the effluent coming out after aerobic treatment is unable to meet the discharge standard. Thus, effluent still contains 2,000–4,000 mg/dm^3 COD and 150–300 mg/dm^3 BOD. The central pollution control board (CPCB) of India and World Health Organization (WHO) has fixed standard for the distillery units to meet the effluent discharge quality, for the release of the wastewater into surface waters ($COD < 0.1\ kg/m^3$, $BOD < 0.03\ kg/m^3$) and sewers ($COD < 0.3\ kg/m^3$, $BOD < 0.1\ kg/m^3$) [2]. Due to this reason, BDE cannot directly be discharged into the water stream without proper treatment. Thus, a comprehensive treatment strategy needs to be implemented to conform to the desired standards.

Various physicochemical treatment methods like wet oxidation [3,4], thermolysis [5,6], and coagulation/flocculation [7] have been reported for the treatment of SW and BDE. In wet oxidation (WO), aqueous waste is oxidized in liquid phase at high temperature (400–573 K) and pressure (0.5 20 MPa) in the presence of air/oxygen. A 60% TOC was reduced from timothy grass–based SW [3]. Catalytic thermolysis of BDE in the presence of CuO catalyst gave 70% COD reduction at 140°C [5]. Dhale and Mahajani [8] has also been suggested a three-step treatment process for BDE having thermal treatment followed by flocculation with an anionic polyelectrolyte. Garg [9] has shown the potential of inorganic salts that act as coagulants/catalysts for the removal of dissolved solids and color of black liquor from pulp and paper mills. Kumar et al. [10] has used a $CuSO_4$, commercial alum, $FeSO_4$, $FeCl_3$, CuO, ZnO, and PAC (poly aluminum chloride), which act as coagulants/catalysts and flocculate at ambient temperature, for the removal of COD and color of composite wastewater from a cotton textile mill. Iron and aluminum salts [7] have also been used for the coagulation and precipitation of dissolved color and COD from the BDE of a sugar cane–based alcohol distillery.

Chaudhari et al. [11] have shown the potential of $CuSO_4$ as a coagulant/flocculant in the removal of colour and COD of pulp and paper mill effluent. They have shown that under optimal initial pH (pH_i) of 6 and $CuSO_4$ dosage of 5 g/l, about 76% COD removal and 78% colour removal could be obtained.

This article aims to study the use of different coagulants, such as $FeCl_3$, $FeSO_4 \cdot 7H_2O$, $AlCl_3$, alum, and $CuSO_4 \cdot 5H_2O$, for the removal of COD and color from the BDE of rice grain–based alcohol distillery. Effect of pH and coagulant dosages have been studied during the removal of COD and color. The reduction in chloride, phosphate, sulfur, carbohydrate, and protein has also been studied. From the operational point of view, the separation of coagulated/flocculated mixture is very important, and therefore, settling and filtration studies were also conducted. Due to easy availability of coagulants, fast and effective process, it can be applied to treat BDE of rice grain–based distillery effluent. No work on coagulation treatment of rice grain BDE has been reported in open literature.

2. Materials and methods

2.1. Materials

The BDE was obtained from Chhattisgarh Distillery Ltd, Kumhari, C.G. (India). The analysis of the sample is presented in Table 1. Analytical reagent (A.R.) grade chemical was used for the analysis of the parameters. Laboratory reagent (L.R.) grade $FeCl_3$, $FeSO_4.7H_2O$, $AlCl_3$, and $CuSO_4.5H_2O$ chemicals were obtained from Merck Ltd., Mumbai (India). Commercial grade alum was arranged from municipal water treatment plant, Raipur, Chhattisgarh. The characteristics of coagulants are given in Table 2. A Wattman filter paper was supplied by GE Healthcare Ltd, Buckinghamshire (UK).

2.2. Experimental method

About 0.5 dm^3 of BDE was taken in a 1-dm^3 glass beaker. The known amount of coagulant was added to the effluent and mixed with the help of glass stirrer. The pH of effluent was noted, and initial pH (pH_i) was adjusted by adding aqueous NaOH (2 M) or H_2SO_4 (2 M) solution and kept on jar test apparatus for coagulation process. The coagulant added BDE was mixed for 15 min with the help of paddle stirrer at 100 rpm, after this it was slowly mixed (40 rpm) for 5 min. When the process was completed, the glass beaker was kept quiescent for about 5 h, and the supernatant liquor was taken for COD and color analysis. The steps were repeated for different coagulant dosages. Settling study was performed in 0.5 dm^3 measuring cylinder.

Table 1
Typical composition of biodigester effluent and the coagulant treated BDE

Parameters	Biodigester effluent	Alum (60 mM)	$AlCl_3$ (60 mM)	$FeCl_3$ (60 mM)	$FeSO_4$ (60 mM)	$CuSO_4$ (60 mM)
COD	13,600	2,040	4,352	2,992	1,632	1,224
TDS	46,245	15,964	11,958	17,738	16,678	9,936
TSS	30,000	17,069	11,631	12,460	12,330	10,606
TS	76,245	33,033	23,589	30,198	29,008	20,542
Reduced carbohydrate	416	–	–	–	–	–
Protein	185	145	80	100	112	55
Chloride	124	230	762	1,418	100	117
Phosphate	0.06	0.15	0.1	0.35	0.12	0.08
Total hardness	9,200	3,000	1,300	1,800	4,500	6,200
Sulphate	4,920	12,365	8,250	12,830	17,220	19,014
pH	7.8	5.0	6.0	5.0	5.0	6.0
Color	Blakish brown	Greenish yellow	White	Greenish brown	Brownish yellow	Light blue
Absorbence at $\lambda = 475$ nm	0.186	0.037	0.049	0.037	0.035	0.033
Color (PCU)	450	87	116.75	84.67	84.67	79.83

Table 2
Characteristic of $CuSO_4$, Alum, $FeCl_3$, $AlCl_3$, and $FeSO_4$

Characteristic	$CuSO_4{\cdot}5H_2O$	Alum	$FeCl_3$	$AlCl_3$	$FeSO_4{\cdot}7H_2O$
Appearance	Bluish solid	White solid	Brownish yellow solid	Light yellow solid	Brownish yellow solid
Lead	Nil	Nil	Nil	Nil	0.0005%
Al/Fe/Cu content	0.255	0.156	0.348	0.204	0.201
Iron	0.05%	0.37	–	0.05%	0.05%
Sulphate	–	–	Nil	.01%	–
pH of 1% solution	4.24	1.94	0.78	2.77	3.23

2.3. *Analytical procedure*

The COD of the sample was determined by the close reflux method. The samples were digested at 148°C, and then, their absorbance was determined at 605 nm. Sulfate and phosphate contents were determined by standard methods [12]. Protein was estimated by Lowry method [13] Strength of the chloride in the sample was determined by standard titrametric method [14]. The reduced carbohydrate was estimated by Fehling's method [15]. pH of the sample was determined using a digital pH meter (EI Made, India). The color of the samples was measured in terms of the observance at $\lambda = 475$ NM using UV-spectrophotometer (Thermo Fisher, Germany) as reported by Migo et al. [16].

3. Result and discussion

The characteristic of BDE shows (Table 1) reduced carbohydrate, melonoidin, and proteins. The presence of similar components has been reported in molasses-based SW and BDE, but the difference is in their quantities [7]. Carbohydrates provide carboxylic and hydroxyl functional groups. Lignin is in very little amount in rice grain–based BDE. Protein structured by amino acid, which after the neutralization provides negative charge. Melonoidin passes net negative charge [16]. The BDE contains more colloidal particles than SW, and therefore, BDE treatment is better to SW by coagulation process [16,17]. The colloidal surfaces have negative charge. Iron and aluminum salts are most widely used coagulants and is trivalent in nature. Aluminum chloride ($AlCl_3$), alum ($Al_2(SO_4)_3$), and ferric chloride ($FeCl_3$) release metal cations, when they dissolved in aqueous solution. Several monomeric and polymeric species are generated on hydrolysis of these metal cations. In the case of Al salts, monomeric species $Al(OH)^{2+}$, $Al(OH)_2^2+$, $Al_2(OH)_2^4+$, $Al(OH)^{4-}$, and polymeric species $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$ are formed, while Fe salt produces $Fe(OH)^{2+}$, $Fe(OH)_2^{2+}$, $Fe_2(OH)_2^{4+}$, $Fe(OH)^{4-}$, $Fe(H_2O)^{2+}$, $Fe(H_2O)_5OH2^+$, $Fe(H_2O)_4(OH)^{2+}$, $Fe(H_2O)_8(OH)_2^{4+}$, $Fe_2(H_2O)_6(OH)_4^{2+}$ monomeric and polymeric species [18–20]. Copper sulfate releases Cu^{2+} ions in solution. It also forms monomeric and polymeric species. The metal hydroxide polymers posses positive charge, have an amorphous structure with large surface area and are hydrophobic in nature [21]. As they are hydrophobic in nature, it can adsorb and neutralize the organic anionic particles that settle down due to its heavy mass-promoting sweep coagulation [20,22]. The anhydride metals that remain in the cation form also tend to associate with a number of functional groups of organic components present in the wastewater. The negative charges of these functional groups are neutralized by it, resulting in colloidal destabilization and precipitation of the metal (cations)-organic (anions) complex. When the complex settles down due to gravity, it also adsorbs the contaminants (organic and inorganic amorphous floc) [22] along with it. Amorphous $M(OH)_3$ flocs is also formed, which have large surface area that helps in rapid adsorption of soluble organic compounds and trapping of colloidal particles. These flocs are then removed by sedimentation. The general form of the hydrolysis reaction of trivalent metals is as follows [20]:

Aqueous solution

$$\text{Salts} \rightarrow \text{Metal cations} + \text{Anions } (Cl^-, NO_3^-, SO_4 \text{ etc.}) \tag{1}$$

$$xM^{3+} + yH_2O \rightarrow Mx(OH)_y^{(3x-y)+} + yH^+ \tag{2}$$

3.1 Effect of pH

The initial pH has been found to have a major effect on coagulation process. At different pH, experiments were conducted to study the effect on the reduction of the COD and color of BDE, with different coagulants. pH was varied from pH 2 to pH 10. The results are presented in Fig. 1. When $FeSO_4{\cdot}7H_2O$ was used as a coagulant, it was found that the COD reduction of BDE increases with an increase in pH from 2 to 5. A decreasing trend was observed from pH 5 to 6 and the COD reduction again increased in the pH range of 6 to 7 and after pH 7 it decreases. A maximum of 88% COD reduction was achieved at pH 5, using $FeSO_4{\cdot}7H_2O$. From the Fig. 1(b), it is clear that the color removal of 80% was maximum at pH 5, and further, it decreased with any variation in pH. The coagulant $AlCl_3$ gave 68% COD and 73% color reduction at pH 6. The COD reduction with coagulant $AlCl_3$ increased from pH 2 to 6, and thereafter, it decreased till pH 8, after that slightly increase was observed up to pH 10 (47% COD reduction).

While using alum, a maximum of 85% COD reduction and 80% color reduction was obtained at pH 5. Any variation from pH 5, the COD and color removal efficiency reduces. Trend of COD reduction was observed was $pH_i < 5$ and $5.5 \leq pH_i \leq 7$. Further increase in pH_i showed an increase in COD reduction. Alum showed better result as compared to $AlCl_3$. This may be due to the hydrolysis of alum. Aluminum hydroxides are produced on the hydrolysis of alum, which forms amorphous and gelatinous flocs responsible for the sweep coagulation. The gelatinous flocks were not observed in case of coagulation with $AlCl_3$.

$CuSO_4{\cdot}5H_2O$ showed very good results. At pH 6 and 60 mM coagulant dosage, 91% COD reduction and 81.8% color reduction were achieved. This may be due to the presence of more unfilled orbital in Cu. The anionic compounds of wastewater act as a good complexing agent and electron donor to the Cu. A decreasing trend of COD and color reduction was observed for $pH_i < 6$ and $pH_i > 6$. With $FeCl_3$ coagulant 78% COD and 80% color reduction were observed at pH 5. COD reduction decreased for $pH_i < 5$ and $pH_i > 5$. The gelatinous flocs were not observed, when $FeCl_3$ coagulant was used.

The decolorization is expressed as the percent decrease in the absorbance of the treated BDE sample from the untreated sample at $\lambda = 475$ nm [16]. The decolorization is due to the removal of melanoidin, and other organic components that separate out from the effluent during coagulation.

Coagulants such as $FeCl_3$, $AlCl_3$, alum, $FeSO_4{\cdot}7H_2O$, and $CuSO_4{\cdot}5H_2O$ are acidic in nature. The addition of these coagulants alters the original pH value of the BDE during coagulation process. From the Fig. 1(a) and (b), it is also clear that every coagulant has a unique optimum pH, and any variation from the pH can appreciably influence the final result of the experiment. The formation of metal hydroxide cations, metal hydroxides, and metal cations are governed by the pH of the solution. The quantity and quality of these species contributes the two mechanisms of coagulation, the charge neutralization and the sweep flocculation. Charges of functional groups present in the effluent also varied with pH [23]. The optimum pH was found to be 5, 6, 5, 5, and 6 for $FeCl_3$, $AlCl_3$, alum, $FeSO_4{\cdot}7H_2O$, and $CuSO_4{\cdot}5H_2O$, respectively. At the optimum pH and coagulant dosages, color reductions are less as compared to COD reductions. This may be due to the presence of numbers of microparticle that are

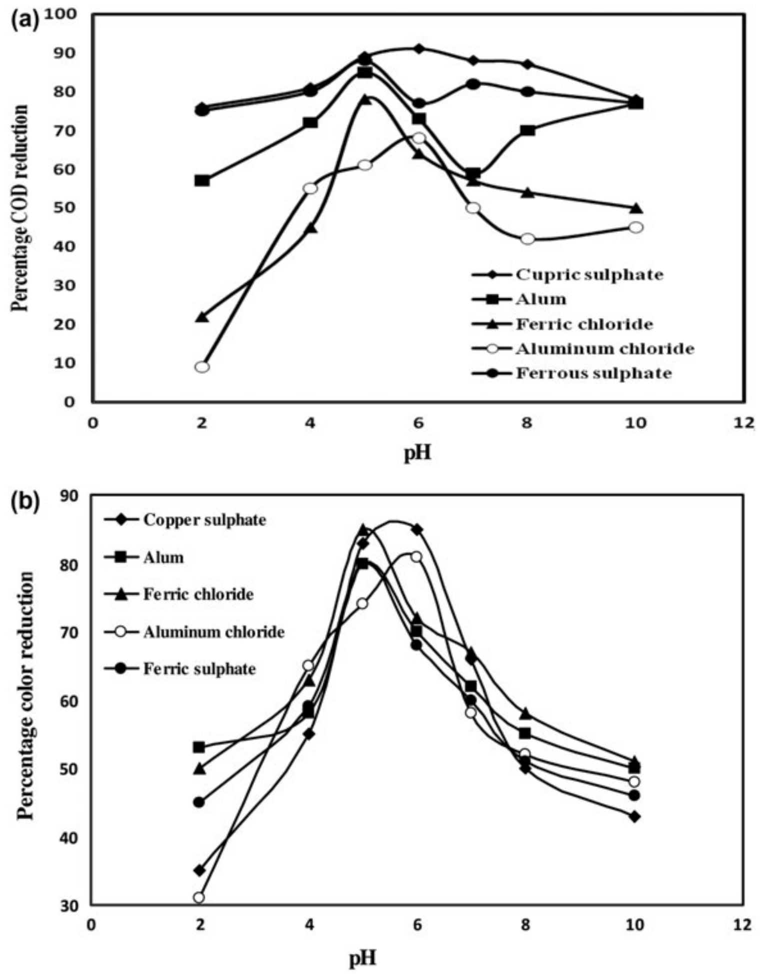

Fig. 1. Effect of pH_i (a) COD reduction (b) color reduction of BDE using different coagulants. $COD_i = 13{,}600\,mg/dm^3$, $C_W = 60\,mM$.

still present in the effluent-treated water that imparts color to the treated effluent [24].

3.2. Effect of coagulant dosages

Study of optimum coagulant dosage for different coagulants, for the reduction of COD and color is an another important parameter. In the present study, different dosage of $FeCl_3$, $AlCl_3$, alum, $FeSO_4.7H_2O$, and $CuSO_4.5H_2O$ was used. The results obtained are presented in Fig. 2(a) and (b). Percentage COD reduction obtained with 30 mM (Al^{3+}) aluminum chloride, (Fe^{3+}) ferric chloride, (Al^{3+}) alum, (Fe^{2+}) ferrous sulfate, and (Cu^{2+}) copper sulfate were 58, 66, 70, 80, and 81%, respectively. The percentage COD reduction increased continuously to 68, 78, 85, 88, and 91%, respectively, when coagulant dosages were increased to 60 mm from 30 mm. When further the coagulant dosage was increased from 60 mM, for all five coagulants, the COD reduction decreased. This is due to restabilization of neutralized organic anions at higher doses of coagulants [23]. Similar effects were also observed for the treatment of pulp and paper effluent by coagulation process [24].

The color reduction of BDE with coagulants mass loading is presented in Fig. 2(b). Color reduction of 85% was obtained with $CuSO_4{\cdot}5H_2O$ as a coagulant and at an optimum dosage of 60 mm Cu^{2+}. The values of color reduction decrease with the addition or reduction of the coagulant dosage. The optimum color reductions were in the order of 78, 85, 70, and 79% for alum, $FeCl_3$, $AlCl_3$, and $FeSO_4{\cdot}7H_2O$, respectively, at their optimum loading 60 mm of coagulant dosing. With the increase in coagulant dosages from 30 to 60 mM, the color reduction increases. With further increase in dosages, the color reduction decreases. The

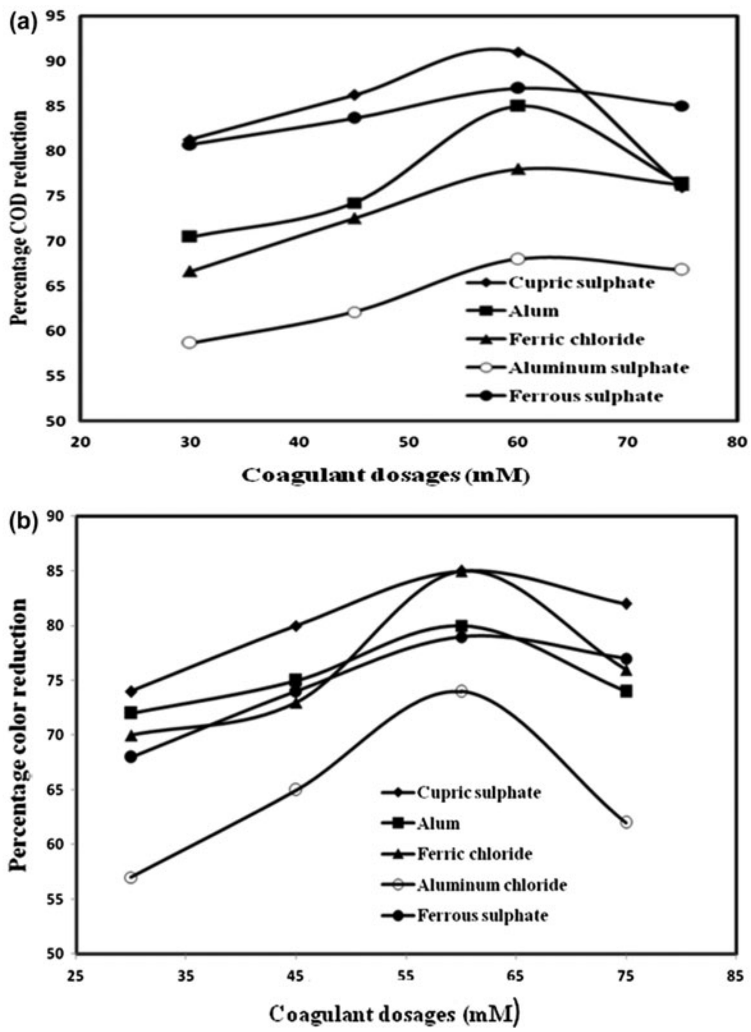

Fig. 2. Effect of coagulant doze on (a) COD reduction (b) color reduction of BDE at optimum pH using different coagulants. COD_i = 13,600 mg/dm^3, $color_i$ = 450 PCU.

increase in coagulant dosages up to certain limit results in the formation of more metal cations, metal hydroxide cations and also more neutralized metal hydroxide. These results in increase in the COD and color reduction. Higher dosages of coagulants destabilize and neutralize the organic anions thereby aiding in higher color intensity.

The effect of coagulant dosage on variation of original pH of BDE is shown in Fig. 3. It was seen that coagulants are acidic in nature. The acidic nature is in the order of $Fe^{3+} > Al^{3+} > Cu^{2+}$, as shown in Table 2. When coagulants are added in the BDE, the pH of the original BDE reduces. The original pH of BDE was 7.8. On addition of 30 mM $CuSO_4 \cdot 5H_2O$ in the BDE, the pH of the BDE was reduced to 7.3 pH of BDE which continued to fall with further increase in coagulant dosage. With the addition of 90 mM (Cu^{2+}) $CuSO_4 \cdot 5H_2O$ in BDE, the pH of the BDE becomes 2.1. Similarly, when $FeCl_3$, $AlCl_3$, alum, and $FeSO_4 \cdot 7H_2O$ was used as coagulant, the pH after the addition of coagulant dosage of 30 mM was 6.8, 7.2, 7, and 6.5. The pH further reduced to 2, 2.6, 2.5, and 2.1, respectively, with 90 mM. The reason for decrease in pH is due to the metal cation and metal hydroxide cations, which enhances the acidity of the BDE. It has been observed earlier that coagulants, such as $FeCl_3$, $AlCl_3$, alum, $FeSO_4 \cdot 7H_2O$, and $CuSO_4 \cdot 5H_2O$, gave optimum COD and color reductions at pH 5, 6, 5, 5, and 6 with 60 mM coagulant mass loading. So addition of some alkali is required to maintain the pH. Alum as a coagulant, works best at pH 5 with optimum dosage 60 mM, thus alkali addition is not

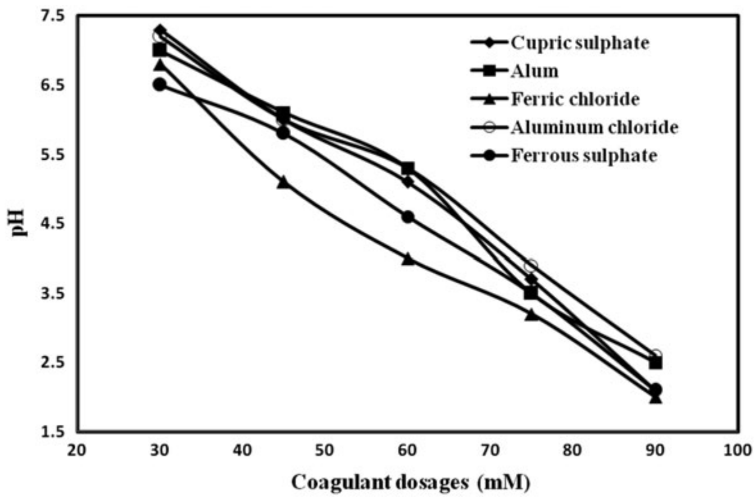

Fig. 3. Effect of coagulant doze on the variation of pH of BDE, $pH_i = 8.0$.

required in this case. While in the case of $CuSO_4$, after the addition of 60 mM coagulant dosage the pH decreased to 5.2.

3.3 Settling studies of the treated effluent

It is necessary to separate the sludge and liquid contents of the slurry mixture by sedimentation process. Sedimentation is one of the economical method compared with other separation processes. To study the separation characteristic by settling, the BDE after the coagulation process was slowly mixed and taken in 0.5 dm^3 cylinder having a diameter of 4.6 cm. The supernatant and solid interphase was noted with time. Fig. 4 shows the time versus height graph of settling sludge for different coagulants. It is seen that the settling of the solids is faster initially and after some time, it decreases. The portion in which settling is faster is known as zone-settling region and the portion where a compressed layer begins to form at the bottom of the cylinder is called compression settling region. The settling rate was found in the order of Alum > $FeSO_4·7H_2O$ > $FeCl_3$ > $AlCl_3$ > $CuSO_4·5H_2O$. Alum showed best settling rate as compared to other coagulants. This may be due to the formation of amorphous, gelatinous, heavy flocks, which duly settled due to gravity. Colloids may entrap in flocs as it is formed or enmeshed in sticky surface as the flocs gets settled. It has been also observed that iron-based coagulants make heavy flocs as compared to aluminum-based coagulant. Hence coagulation with alum and $FeSO_4·7H_2O$ is a good choice for COD reduction and sludge separation. The COD reduction of 85% and 88% obtained with alum and $FeSO_4·7H_2O$ coagulant, respectively. In sedimentation studies, batch sedimentation data are of immense importance. Using the batch sedimentation data, a continuous thickener may be designed [25–27]. The method proposed by Richardson et al. [25] is common to design a continuous thickener based on batch studies.

3.4 Filterability

Due to the coagulation/flocculation process, small colloidal particles agglomerate and hence effective size of the particles increases. For the separation of such agglomerate, the particle filtration method is one of the options. Constant pressure filtration was applied in this study. Parameters such as filtration resistance of the filter media and filter cake resistance were calculated using the filtration equation [29].

$$\frac{dt}{dv} = k_p V + \beta \tag{3}$$

$$K_p = \frac{C\alpha\mu}{A^2(-\Delta p)} \tag{4}$$

and

$$\beta = \frac{\mu Rm}{A(-\Delta p)} \tag{5}$$

where t is the time taken of filtration (s), V is the volume of the filtrate collected in t time (m^3), k_p is the

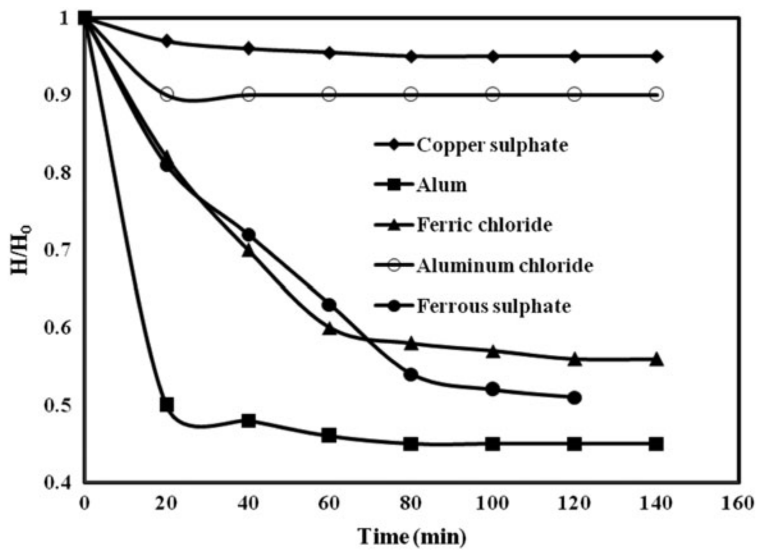

Fig. 4 Settling characteristic of the coagulated slurry.

slope of the plot of Eq. (1) (s/m^6), β is the intercept for the plot of Eq. (3) (s/m^3), C is the concentration of sludge (kg/m^3), α is the specific cake resistance (m/kg), μ is the viscosity of the filtrate (Pa s), A is the area of the filter media (m^2), Δp is the pressure drop across the filter (Pa), and R_m is the filter medium resistance (m^{-1}).

To study the filtration characteristic of treated BDE, gravity filtration was performed on Wattman filter paper supported on a Buchner funnel. The filtration experiment was conducted at ambient temperature (29 ± 3℃) and at atmospheric pressure (101.3 kpa). The experimental data were plotted as (dt/dv) vs. V as shown in Fig. 5. The value of k_p(slope) and β (intercept) was determined by the best fit method of the experimental data. The evaluated data are presented in Table 3. The cake resistance was found in the order of $146 \times 10^{13} > 127 \times 10^{13} > 74 \times 10^{13} > 32.6 \times 10^{13}$ (m/kg) for $AlCl_3$, alum, $CuSO_4$ and $FeCl_3$-treated BDE, respectively. These shows that BDE treated by the coagulant $FeCl_3$ is easy to filter as compared to other coagulant-treated BDE. The reason for the variation in cake resistance is due to the porosity of the cake which seemed to be highest for $FeCl_3$ and lowest for $AlCl_3$. The filter medium resistance in decreasing order was found to be 22.84×10^8, 16.06×10^8, 11.74×10^8, and 7.25×10^8 m^{-1} for alum, $CuSO_4{\cdot}5H_2O$,- $FeCl_3$-, and $AlCl_3$-treated BDE, respectively. The filter medium resistance is especially important during the early stage of filtration. During filtration, the first drop of filtrate from $AlCl_3$-treated BDE appeared early as compared to other treated BDE. Specific cake resistance values for different sludges have been reported by Barnes et al. [30]. These values are $4–12 \times 10^{13}$ m/kg for the activated sludge and $3–30 \times 10^{13}$ m/kg for the digested sludge. Filtration data were also evaluated for molasses based distillery effluent [7] and textile mill effluent [10].

3.5 Analysis of filtrate

Analysis of the filtrate was carried out for the determination of various parameters, after the treatment of BDE by different coagulants. The results are presented in Table 1. It can be observed that large amount of COD (13,600 to 1,224 mg/dm^3) was reduced after the coagulation/flocculation process. The COD is responsible for high organic load in the stream. It can be also seen that color of the BDE reduced up to 82%. Reduced carbohydrate, proteins, chloride, phosphate, sulfate, total hardness, and total solids were also satisfactorily reduced from the BDE. Fig. 6 also shows that after treatment many functional groups and chemicals (organic and inorganic) are reduced from the BDE. The absorbance has been found to decrease when the treated BDE was scanned by UV spectrophotometer in the range of 200–700 nm wavelength. $CuSO_4{\cdot}5H_2O$ and alum were found to be a better coagulant as compared to other coagulant such as $FeCl_3$, $AlCl_3$, and $FeSO_4{\cdot}7H_2O$. In this process, most of coagulant metals and metal hydroxide cations make complexes with pollutants having a negative charge. Small amounts that remain in the treated

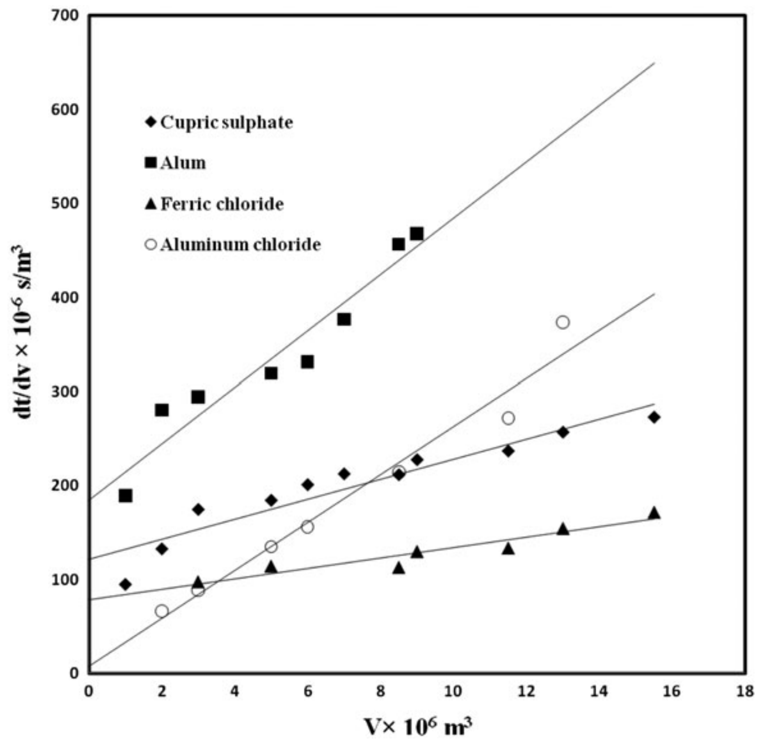

Fig. 5. Filterability of the flocculated slurry. $CuSO_4·5H_2O$ (pH_i 6), alum (pH_i 5), $AlCl_3$(pH_i 6), and $FeSO_4·5H_2O$ (pH_i 5).

Table 3
Filterability of treated BDE

Coagulant	$K_p \times 10^{-12}$ (s/m^6)	$\beta \times 10^{-6}$ (s/m^3)	C (kg/m^3)	$\mu \times 10^3$ (PaS)	$\alpha \times 10^{-13}$ (m/kg)	Rm × 10^{-8} (m^{-1})
$CuSO_4$	11.48	110	22.43	1.023	74	16.06
Alum	31.25	185	30.31	1.21	127	22.84
$FeSO_4·7H_2O$	5.96	80	26.78	1.018	32.6	11.74
$AlCl_3$	28.37	5	28.15	1.03	146	7.25

water depends on its solubility at different pH [7]. The results of treatment show that the COD reduction does not touch the required level to be discharged into sewers directly (1,224–4,352 mg/dm^3). Also, the effluent after treatment still has color, which is not reduced to the required level. Therefore, further treatment of coagulated treated BDE will be required. The wet oxidation, adsorption, membrane separation processes is possible alternative to treat the effluent after coagulation process. Dissolved metal can work as a catalyst for the wet oxidation process. At present, many industries treat the BDE (COD 13,000–18.000 mg/dm^3) directly using the membrane separation technique, so that treated BDE can be recycled or reused. A good practice may be BDE initially treated by coagulation and then by the membrane separation process. Dissolved coagulant cations could be also removed in membrane separation process along with organics.

3.6 Analysis of residue

Further characterization was done after the separation of solid residues from the treated BDE. Residues of different coagulant were dried at 115˚C and then analyzed. The data of analysis are presented in Table 4. It was found that the weight of alum-treated residue was highest. Color and the approximated drying period was different for different sludge. The nature of the residues was found to be hard and difficult to grind. It has been reported that coagulant-treated organic residues may posses good heating value [7,10].

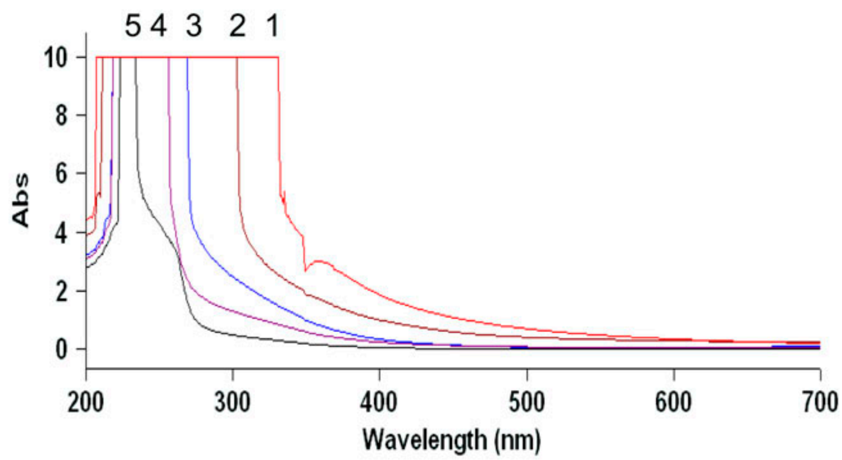

Fig. 6. Absorbance of BDE and treated BDE as a function of wavelength.
Note: **5**__ CuSO4.5H2O, 3__ $AlCl_3$, **4**_ **$FeCl_3$,** 2__Alum, 1__BDE

Table 4
Analysis of residue obtained after coagulation

Coagulant	$CuSO_4{\cdot}5H_2O$ (60 mM)	Alum (60 mM)	$FeCl_3$ (60 mM)	$AlCl_3$ (60 mM)	$FeSO_4{\cdot}7H_2O$ (60 mM)
Initial pH (pH_0)	6	5	5	6	5
Weight of residue (kg/m^3)	22.43	30.31	26.78	28.15	24.64
Color	Blue	Brown	Dark brown	Dark brown	Brown
Nature	Bulky mass, difficult to grinding	Bulky mass, difficult to grinding	Bulky mass, difficult to grinding	Bulky mass, difficult to grinding	Bulky mass, difficult to grinding
Approximated drying period	9	14	11	15	10
% convertible COD	91	85	78	68	88

4. Conclusion

Coagulation/flocculation process for the treatment of BDE of a rice grain–based distillery is an effective treatment method to reduce its COD and color. $FeCl_3$, alum, $AlCl_3$, $FeSO_4.7H_2O$, and $CuSO_4{\cdot}5H_2O$ used as coagulant reduced the COD of the BDE to 78, 85, 68, 88, and 91% and color to 80, 80.46, 73, 80, and 81.8%, at their optimum pH of 5, 5, 6, 5, and 6, respectively. The pH of the BDE played a significant role. The COD and color reduction was found to increase considerably with the increase in the dosages of coagulants up to a certain limit (up to 60 mM). When dosage was further increased from 60 mM, the percentage reduction of COD was not found to increase further.

The settling characteristic of alum-treated BDE was found best among effluents treated with $FeCl_3$, alum, $AlCl_3$, $FeSO_4{\cdot}7H_2O$, and $CuSO_4{\cdot}5H_2O$. Flirtation studies showed that BDE treated with coagulants have good filterability. Complete removal of COD and BOD from the BDE was not possible by the coagulation/flocculation method. This implies that further treatment of the effluent from coagulation process can be carried out by using aeration, wet oxidation, adsorption, or membrane separation.

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