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Treatment of rice grain based biodigester distillery effluent (BDE) using inorganic coagulants

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The removal of COD and colour from biodigester effluent (BDE) of rice grain based alcohol distillery plant has been studied using inorganic coagulant such as $CaCO_3$, $CuNO_3$ and Na_2SiO_3. $CuNO_3$ is found to be more effective, among all coagulant. COD reduction of 78, 83 and 51% and colour reduction of 75, 78 and 41% is obtained using 60 mM $CaCO_3$, 40 mM $CuNO_3$ and 40 mM Na_2SiO_3 respectively, at their optimum initial pH_i. The pH of effluent-coagulant mixture play a major role in removal of pollutant from the BDE. $CuNO_3$ gives 83% COD reduction and 78% colour reduction along with good settling property. 82% settling occurred with alum in 25 min. The properties of filtrate and residues have also been analyzed.

Keywords: Rice grain based biodigester effluent, Chemical oxygen demand, Settling, Coagulation, Copper nitrate

Alcohol is produced in distilleries by fermentation of sugar cane juice, sugar cane molasses, sugar beet, rice grains, etc. Demand of alcohol is increasing day by day in the field of energy and pharma sector. In India more than 70% ethanol is produced by sugar cane molasses[1] but India is the largest rice producing country in the world, therefore it may be used as a major supplementary raw material for distillery industries at the place of molasses.

Ethanol is produced by fermentation of raw material in fermentation broth. The fermentation broth containing 6-10% alcohol by volume is distilled to recover alcohol remaining is the waste called spent wash (SW). The characteristic of SW depends on raw material and process being used by the industries. For example, effluent from the sugar cane molasses based distilleries have very high COD (i.e. 90000-150000 mg/dm^3)[2], on the other hand SW from timothy grass based distillery contains COD 26000-50000 mg/dm^3 reported by Belkacemi *et al.*[3] Grapes based distillery units SW have COD 22000-48000 mg/dm^3 reported by Wolmarans *et al.*[4] .

The rice grain based SW also contains high COD (35,000-50,000) mg/dm^3 and BOD (7000-10,000) mg/dm^3, and it is sent to the biodigester for anaerobic treatment. Biodigester can reduce 60 to 75 percent COD and 65 to 80% BOD from the spent wash. The output of biodigester called BDE is dark brown in colour, due to the presence of melanoidin and other compound like proteins, waxes and carbohydrates, etc which contributes to COD (10,000-14,000) mg/dm^3 and BOD (1,500-3,000) mg/dm^3. Due to this reason BDE cannot directly be discharged into the stream without proper treatment. The BDE is further treated aerobically to reduce COD and BOD, efficiency of which goes maximum up to 80%, and it is far away from the effluent discharge standard of central pollution control board (CPCB). Generally they prefer COD value of 250 mg/dm^3 and BOD value of 30 mg/dm^3 for the industries discharge in sewers[5]. Hence removal of COD and colour are necessary from BDE.

Various physicochemical treatment methods like wet oxidation[6,7], thermolysis[8,9], adsorption[10] have been reported for the treatment of SW and BDE. These processes have several drawbacks. Thermolysis and wet oxidation process need rigorous operating condition and also it is not cost intensive. Adsorption process does not give very effective results.

Prajapati *et al.*[11] have reported the potential of $CuSO_4 \cdot 5H_2O$, Alum, $FeCl_3$, $AlCl_3$, and $FeSO_4 \cdot 7H_2O$ as a coagulant to remove COD and colour from BDE of rice grain based alcohol distillery. They achieved 78, 85, 68, 88, and 91% COD and 80, 80.46, 73, 80, and 81.8% colour reduction with alum, $AlCl_3$, $FeSO_4.7H_2O$, and $CuSO_4{\cdot}5H_2O$ at their optimum condition. The detailed literature report is presented in Table 1.

This paper deals with the use of various coagulants such as $CaCO_3$, $CuNO_3$ and Na_2SiO_3 for the removal of COD and color from the BDE of rice grain based alcohol distillery. The reduction in chloride, phosphate, sulphur, carbohydrate, protein has been also calculated at their optimum *p*H. Settling studies have been also conducted.

Experimental Section

Materials

The BDE was obtained from Chhattisgarh Distillery Ltd Kumhari, C.G. (India). The analysis of sample is presented in Table 2. Laboratory grade reagent (L.R.) $CaCO_3$, $CuNO_3$ and Na_2SiO_3 were obtained from Merck India Ltd,, Mumbai (India). Whatman filter paper was supplied by GE Healthcare Ltd, Buckinghamshire (U.K).

Experimental method

BDE (0.5 $dm^{3)}$ was taken in a 1 dm^3 glass beaker. A known amount of coagulant was added to the effluent and mixed with the help of glass stirrer. The *p*H of effluent was noted and initial *p*H (pH_i) was adjusted by adding aqueous NaOH (2M) or H_2SO_4 (2M) 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. After the mixing process was complete the glass beaker was kept quiescent for about 4 h. Later on the supernatant liquor was filtered by Whatman filter paper (no 41) and its COD and colour value was analyzed. The steps were repeated for different

Table 2 — Typical composition of biodigester effluent and the coagulant treated BDE

Parameters	Biodigester effluent	$CuNO_3$ (40 mM)	$CaCO_3$ (60 mM)	NaSi (40Mm)
COD	11500	1955	2530	5635
TDS	43245	12964	14198	16738
TSS	39331	14039	15513	17160
TS	82576	27003	29711	33898
Reduced carbohydrate	517	-	-	-
Protein	165	105.2	113.5	120.3
Chlorine	161	106.8	112.1	117.4
Phosphate	0.05	0.15	0.1	0.35
Total hardness	10220	4130	1744	1612
Sulphate	4718	2312	2509	2704
*p*H	7.8	6.5	2.5	4.5
Colour	Blackish brown	Greenish yellow	White	light brown
Absorbence at λ=475 nm	0.831	0.1828	0.2077	0.4903
Colour (PCU)	398	87.56	99.5	234.82

*All value in mg/dm^3 except pH, absorbance and colour

Table 1 — Characteristic of DWW and the coagulation/flocculation treated effluent

Investigator	Substrate	Coagulant	% COD/TOC removal	% Colour removal
Migo *et al.* (1993)	Molasses based	Polyferric hydroxysulphate (PFS)		
	SW		21	32
	BDE		73	87
	LE		73	94
	(TOC Removal)			
Chaudhari *et al.* (2005)	Molasses based BDECOD= 34000	Poly aluminum chloride (PAC)	72.5%	92
		Aluminum chloride ($AlCl_3$)	60%	86
Prasad (2009)	Molasses based diluted SW	Ferric chloride ($FeCl_3$)	55%	83
			NR	67
	COD = 10000 - 11000	MOC		
Prajapati *et al.* (2014)	Rice grain based BDE COD=13,600		91	81.8
			68	73
		Coppr sulphate ($CuSO_4$)	78	80
		Aluminum chloride ($AlCl_3$)	85	80
		Ferric chloride ($FeCl_3$)		
		Alum	85	80.64
		Ferric sulfate ($FeSO_4$)		

Note: All values observed in optimum condition, COD in mg/dm^3

coagulant dosages. Settling study was performed in 0.5 dm^3 measuring cylinder.

Analytical procedure

The COD of the sample was determined by the close reflux method[12]. Sulphate and phosphate contents were determined by standard methods[12]. Protein was estimated by Lowry method[13]. Strength of the chlorine in sample was determined by standard titrametric method[14]. The reduced carbohydrate was estimated by Fehling method[15]. *p*H of sample was determined by using digital *p*H meter (EI Make, India). The colour of the samples were measured in terms of the absorbance at λ=475 nm using UV-spectrophotometer (Thermo Fisher, Germany)[16].

Results and Discussion

The characteristic of BDE shows (Table 2) reduced carbohydrate, melanoidin and proteins. The presence of similar components have been reported in molasses based SW and BDE, but they differ in their quantities[17]. 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 provide negative charge. Melanoidin also posses net negative charge[16]. The BDE contain more colloidal particles than SW, therefore BDE treatment is better option to treat SW by coagulation process[11]. The colloidal surfaces have negative charge. In the experiments coagulants like $CaCO_3$, $CuNO_3$, and Na_2SiO_3 were used to treat BDE. When $CaCO_3$ was added in BDE it released Ca^+ ions, similarly Na_2SiO_3 released Na^+ ions, which gets attached to the negative ions of BDE. Coagulant ions undergo hydrolysis and generate several monomeric and polymeric species.

Copper nitrate releases number of Cu^{2+} ions. It also forms monomeric and polymeric species. The metal hydroxide polymers have been found to possess positive charge amorphous structure with large surface area and are hydrophobic in nature[18]. As they are hydrophobic in nature it adsorbs and neutralizes the organic anionic particles which settle down due to its heavy mass, further promoting sweep coagulation[19]. The anhydride metals remains in the cation form also tends to associate with a number of functional groups of organic components contained in 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 flock) along with it. Amorphous $M(OH)_3$ flocs are also formed, which have large surface area that helps in rapid adsorption of soluble organic compounds and trapping of colloidal particles. These flocs are removed by sedimentation. The general form of hydrolysis reaction of trivalent metals is given as[16]:

Aqueous solution

Coagulants => Compound cations + Anions (CO_3^-, NO_3^-, SO_4 etc) ... (1)

$$xM^{3+} + yH_2O \rightarrow Mx(OH)y^{(3x-y)+} + yH^+ \quad \text{... (2)}$$

Effect of *p*H

The initial *p*H has been found to have tremendous effect on coagulation process; therefore, the COD and colour reduction of BDE with coagulant calcium carbonate at different *p*H were studied with *p*H variation from *p*H 1.5 to 10.5. It was found that 75, 78, 60, 66, 69 and 62% COD reduction and 67, 75, 52, 61, 63 and 56% colour reduction were achieved at *p*H 1.5, 2.5, 4.5, 6.5, 8.5 and 10.5 and are presented in Fig. 1 and Fig. 2. Copper nitrate is an important coagulant to treat BDE. After treatment results showed 58, 66, 83, 71 and 67% COD reduction and 51, 59, 78, 67 and 63%, colour reduction at *p*H 2.5, 4.5, 6.5, 8.5 and 10.5. Any variation from *p*H 6.5, the COD and colour removal efficiency was reduced.

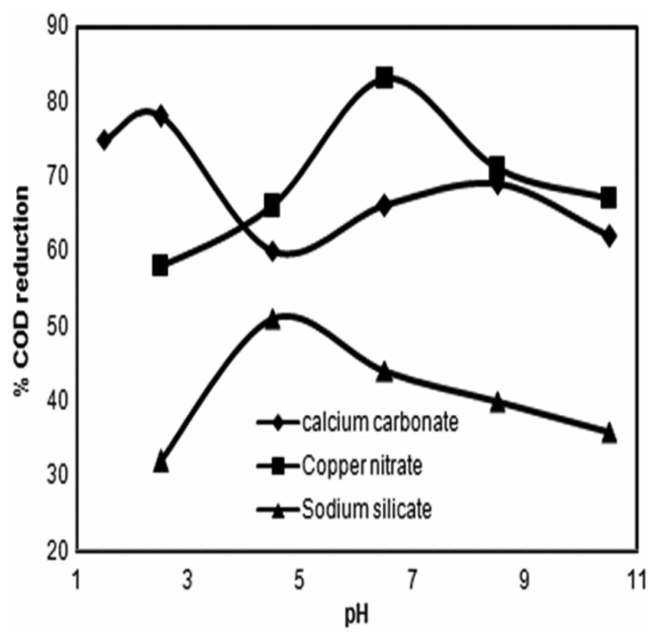

Fig. 1 — Effect of pH_i COD reduction of BDE using different coagulants. $CaCO_3$ = 60 mM, $CuNO_3$ = 40 mM, NaSi = 40 mM

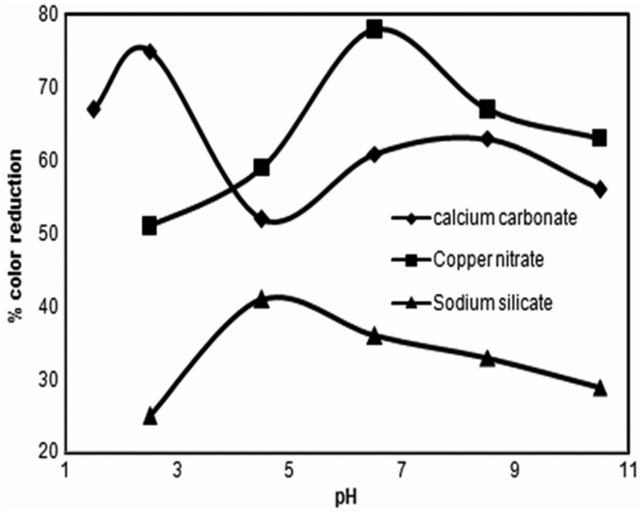

Fig. 2 — Effect of pH_i on colour reduction of BDE using different coagulants. $CaCO_3$ = 60 mM, $CuNO_3$ = 40 mM, NaSi = 40 mM

Decreasing trend of COD reduction was observed for *p*Hi < 2.5 and 6.5< *p*Hi <6.5. Further increase in *p*Hi showed increase in COD reduction. Na_2SiO_3 was also used to treat BDE, COD reduction of 32, 51, 44, 40, 36% and color reduction of 25, 41, 36, 33and 29% with 40 mM coagulant dose and at *p*H 2.5, 4.5, 6.5, 8.5 and 10.5 was achieved. It was seen that COD and colour reduction of the BDE is function of *p*H. This may be due to the reaction rate of coagulant cations depending on the number of H^+ ions generated during the process.

The decolorization is expressed as the percent decrease in the absorbance of the treated BDE sample from the untreated sample at λ = 475 nm[12]. The decolorization is due to removal of melanoidin and other organic components which separates out from the effluent during coagulation.

The formation of compound hydroxide cations are governed by the *p*H of the solution. The quantity and quality of these species contributes the two mechanisms of coagulation charge neutralization and sweep flocculation. Charges on functional groups present in the effluent also vary with *p*H. For the $CaCO_3$, $CuNO_3$ and Na_2SiO_3 the optimum *p*H was 2.5, 5 and 4.5 respectively. At the optimum *p*H and coagulant dosages, COD reductions are less as compared to the colour reductions, because some amount of organic matter were still present in treated water which enhances the COD value.

Effect of coagulant dosages

To get optimum dosage for different coagulants on basis of COD reduction and colour reduction of BDE, different dosage of $CaCO_3$, $CuNO_3$ and Na_2SiO_3 was used during the experiments. The results are presented in Fig. 3 and Fig. 4. The effect of $CaCO_3$ on COD and colour reduction was studied with different coagulants dosages at their optimum *p*H. COD reduction of 35, 53, 78, and 61% and colour reduction of 48, 67, 75 and 68% was achieved, with coagulant dosages of 20, 40, 60 and 80 mM $CaCO_3$.

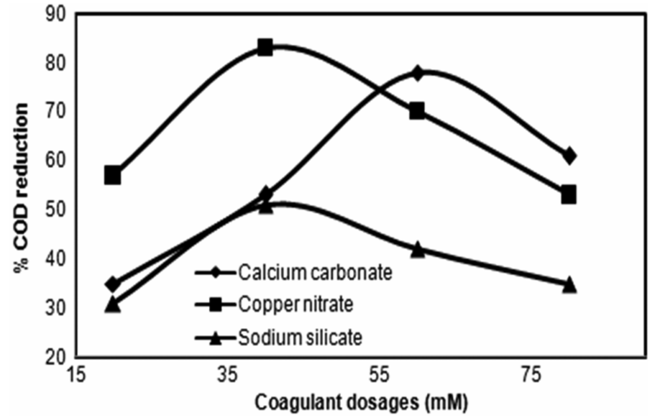

Fig. 3 — Effect of coagulant doze on (a) COD reduction BDE at optimum *p*H using different coagulants. COD_i=11500 mg/dm^3. $CaCO_3$ = *p*H 2.5, $CuNO_3$ = *p*H 6.5, NaSi = *p*H 4.5

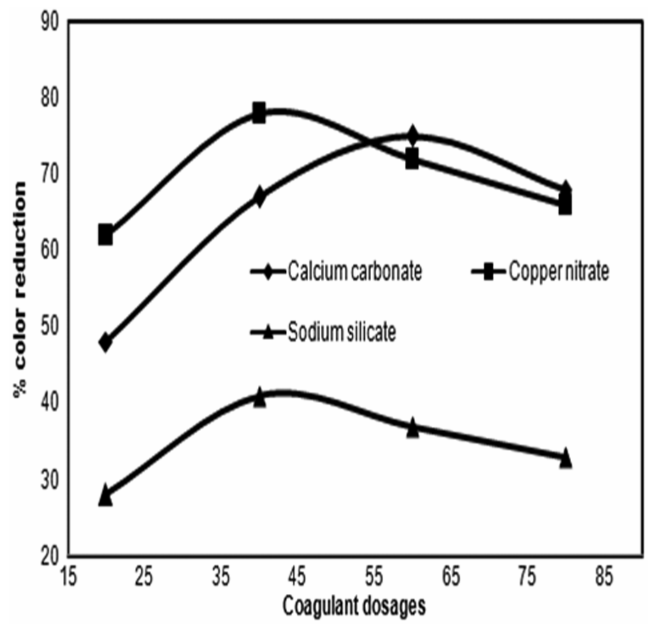

Fig. 4 — Effect of coagulant doze on colour reduction of BDE at optimum *p*H using different coagulants. COD_i=11500 mg/dm^3, $colour_i$ = 430 PCU. $CaCO_3$ = *p*H 2.5, $CuNO_3$ = *p*H 6.5, NaSi = *p*H 4.5

While using copper nitrate, 57, 83, 70 and 53% COD reduction and 62, 78, 72 and 66% colour reduction with coagulant dosages 20, 40, 60 and 80 mM was achieved. It was observed that any variation from coagulant dosage of 40 mM the COD and colour removal efficiency reduced. Decreasing trend of COD reduction was observed for coagulant dosage of 40 mM ≤ coagulant dosage ≤ 40 mM.

Na2SiO3 showed very poor result and 31, 51, 42 , 35 COD reduction and 28, 41, 37, and 33% colour reduction with 40 mM coagulant dosage at the optimum *p*H was achieved.

The increase in coagulant dosages up to certain limit results in formation of more compound cations, compound hydroxide cations and also may be more neutralized compound hydroxide. These resulted in the increase in COD and colour reduction. The high dosages of coagulants destabilize and neutralize the organic anions thereby causing for higher colour intensity.

The effect of coagulant dosage on variation of original *p*H of BDE is shown in Fig. 5. The original *p*H value of the BDE was 7.8 which changed with the addition of coagulants. Coagulants $CaCO_3$ showed neutral characteristic, $CuNO_3$ showed acidic nature and Na_2SiO_3 showed alkaline nature. When 20 mM $CaCO_3$ was added in BDE, the *p*H value reduced to 7.2. Further addition of $CaCO_3$ in the BDE, the *p*H remained nearly the same. Similarly 20 mM $CuNO_3$ reduces the *p*H value of BDE to 4.46 and further increasing the coagulant dosages upto 80 mM the *p*H remains constant. However 20 mM Na_2SiO_3 increases the *p*H value of BDE to 9.38 which increases up to *p*H 12.62 with coagulant dosages of 80 mM.

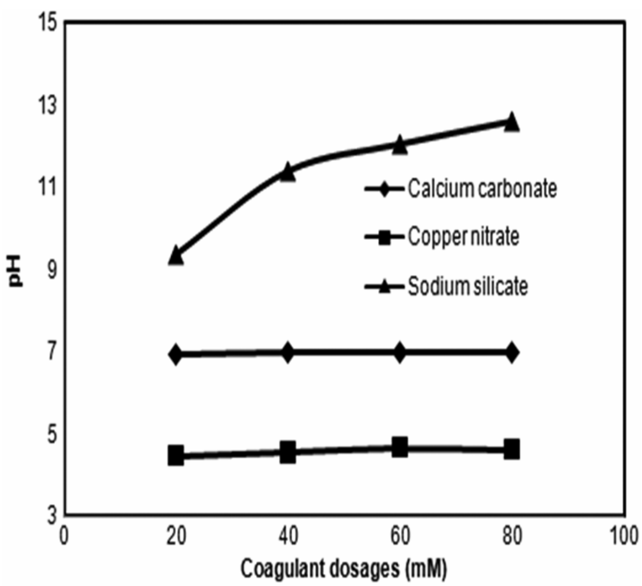

Fig. 5 — Effect of coagulant doze on the variation of *p*H of BDE., pH_i.=8.0

Settling study of the treated effluent

It is necessary to separate the sludge and liquid contents of slurry mixture in sedimentation apparatus. Sedimentation is the most economic method compared to the other separation processes. To study the separation characteristic by settling, the BDE after coagulation process was slowly mixed and taken in 0.5 dm^3 cylinder having diameter 4.6 cm. The supernatant and solid interphase was noted with time. Figure. 6 shows the time Vs height graph of settling sludge of different coagulants. It was observed 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 $CaCO_3$> $CuNO_3$> Na_2SiO_3>. $CaCO_3$ showed better settling but poor COD and color reduction as compared to other coagulant. Several methods have been presented for the evaluation of compression zone depth. Using the batch sedimentation data a continuous thickener may be designed[20]. Method proposed by Richardson *et al.*[20] is common to design a continuous thickener based on batch studies.

Analysis of filtrate

The filtrate was analyzed before and after the treatment of BDE, the result is presented in Table 2. It was observed that large amount of COD was reduced after coagulation/ flocculation process (83% COD reduction using $CuNO_3$). The colour was also reduced up to 78%. Soluble lignin was absent in BDE.

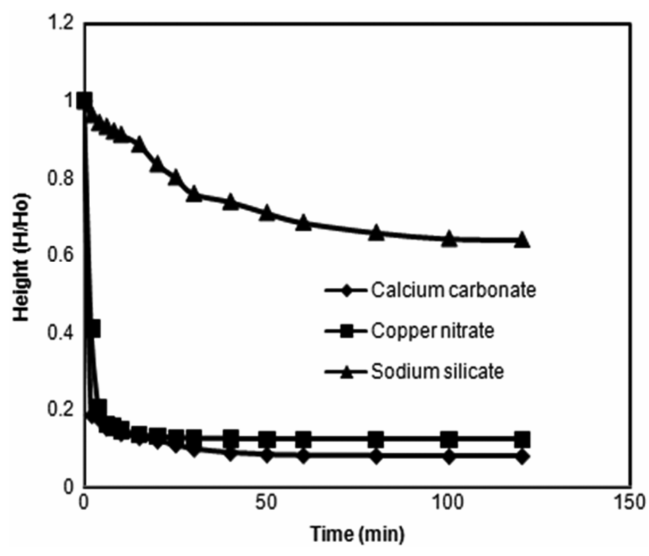

Fig. 6 — Settling characteristic of the coagulated slurry.

Table 3 — Analysis of residue obtained after coagulation

Coagulant	$CuNO_3$ (40 mM)	$CaCO_3$ (60 mM)	NaSi (40Mm)
Initial *p*H(*p*H$_0$)	5	5	6
Weight of residue (kg/m^3)	30.31	15.78	14.15
Colour	Brown	Dark brown	Dark brown
Nature	Bulky mass, difficult to grinding	Bulky mass, difficult to grinding	Bulky mass, difficult to grinding
Approximated drying period	13	10	8
% Convertible COD	83	78	41

Reduced carbohydrate, proteins, chloride, phosphate, sulphate, total hardness and total solid were also reduced up to a satisfactory level from the BDE. Table 1 also shows that after treatment many functional group and chemicals (organic and inorganic) were reduced from the BDE. $CuNO_3$ gave better result (83% COD and 78% colour reduction) as compared to the other coagulant like Na_2SiO_3 and $CaCO_3$. The result shows that the COD (1955-5635 mg/L) and color level does not conform to the dischargeable limit for the treated BDE. The central pollution control board (CPCB), India has norms that the COD of BDE should not greater than 250 mg/dm^3. Hence, further treatment of coagulated treated BDE is necessary. The wet oxidation, membrane separation processes are possible alternate to treat it further so as to reach the dischargeable limit.

Analysis of residue

After the separation of solid residues from the treated BDE, it was further characterized. Residues of different coagulant were dried at 115°C and then analyzed. The data of analysis is presented in Table 3. It was found that the weight of $CuNO_3$ treated residue was highest. Color and approximated drying period was different for different sludge. The nature of the residues were found to be hard and difficult to grind. It has been reported that these organic residues have good heating value[21-23].

Conclusion

Coagulation/flocculation process for treatment of BDE of a rice grain-based distillery is an effective treatment method to reduce its COD and colour. $CuNO_3$, $CaCO_3$ and Na_2SiO_3 gave 83, 78 and 51% COD reduction and 78, 75 and 41% color reduction at their optimum *p*H 6.5, 2.5 and 4.5 respectively. The *p*H of the BDE plays a very significant role. The COD and color reduction was found to increase considerably with the increase in the dosages of coagulants up to certain limit (up to 40-60 mM). Reduction of COD was not found by further increase in coagulant dosage.

The settling characteristic of $CaCO_3$ treated BDE was found to be best among effluents treated with $CuNO_3$ and Na_2SiO_3. Flirtation studied showed treated BDE does have good filterability. Complete removal of COD and BOD from the BDE was not possible by coagulation/ flocculation method. Thus further treatment by using aeration, wet oxidation, and membrane separation can be undertaken.

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