

Decolorization of Anaerobically Digested Molasses Spentwash by Coagulation

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Abstract Treatment of molasses spentwash has always posed a challenge to the environmental engineers. Problem becomes more difficult in the countries like India where more harsh environmental parameters of spentwash on one hand and limitation of treatment cost on the other is crude reality. Inability to grow micro-organisms in undiluted spentwash further limits the options. In this work, various options of coagulation were tried as primary treatment to make spentwash fit for further biological treatment without dilution. Poly aluminium chloride(PAC) was found to be the best coagulant.

Keywords Coagulation, Decolorization, Distillery, Spentwash

1. Introduction

There are about 300 distilleries in India, producing about 2.75 billion litres of alcohol annually[1]. India is the fourth largest producer of ethanol in the world and the second largest in Asia. Though, the alcohol production from starchy material is also practiced on a very limited scale, most of the Indian distilleries use sugarcane molasses as raw material. About 4-10 kg of molasses is required for production of one litre of alcohol[2]. Apart from its use for beverage, medicinal, pharmaceutical and flavouring, alcohol constitutes the feedstock for large number of organic chemicals, which are used in manufacturing a wide variety of intermediates, drugs, rubber, pesticides, solvents etc.[3]. Distillery ranks as the top most industry among the list of 17 heavily polluting industries identified by Ministry of Environment & Forests, Govt. of India, and are covered under Central Action Plan. Distillery spentwash is not only high on organic and inorganic loading, but also has dark brown colour even after industry standard treatment by anaerobic digestion/ bio-methanation. The anaerobically treated spentwash does not meet Central Pollution Control Board(CPCB) standards of discharge into streams or land application. Groundwater colorization is growing concern for areas having land application of distillery spentwash. Spentwash is toxic to aquatic organisms as LC₅₀ value for distillery spentwash was found to be 0.5% for fresh water fish *Cyprinus carpio* var. *Communis*[4]. It behaves much

more hazardingly when disposed into water bodies, since it may result in the complete depletion of dissolved oxygen and aquatic life will be destroyed[5].

Rao et al. conducted laboratory scale studies on methods of removing color from distillery wastewater. Aluminium sulfate and ferric chloride were found very effective in color removal from anaerobically treated diluted molasses and distillery wastes[6]. Color removal of molasses based distillery effluent was studied by Migo et al[7] using a commercial inorganic flocculent, a polymer of ferric hydroxyl sulfate with a chemical formula of $[\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}]_m$. For decolorization of anaerobically digested spentwash combined chemical and biological methods were also tried[8]. The first treatment included calcium oxide and hydrogen peroxide. This was followed by second treatment, which involved hydrogen peroxide and microbes at 144 hrs incubation. Goto et al.[9] reported super critical water oxidation(SCWO) of distillery wastewater for removal of its color. In this process, oxidation reaction took place in water above its critical point(647°K, 22.1 MPa). Experiments were carried out with different amounts of biopolymer chitosan. This gave decolorization of the order of 94% along with 93% reduction in COD. Ten times diluted distillery wastewater(COD as 2800 mg/L) was used for experimentation[10]. Ozonation of distillery(yeast fermented beer) waste was also tried to evaluate the process in terms of organic matter removal and decolorization efficiencies. Ozone generation system used was based on the production of ozone from the reaction of oxygen with UV light[11]. Pikaev et al[12] carried out study on combined electron beam and coagulation method for treatment of molasses based distillery effluent. Nandy et al.

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did their study on a bio-methanation system as pre-treatment option comprising anaerobic fixed film reactors. This was combined with subsequent concentration through Multiple Effect Evaporators(MEE), and concentrated effluent was used for bio-composting of press-mud for production of bio-manure[13]. Color removal from biologically pre-treated molasses spentwash(COD 4580 ± 100 mg/L) by chemical oxidation through ozone was investigated by Pena et al[14].

Electrochemical treatment of digested spentwash was carried out for removal of its color. Power consumption was reported as 1.13-4.93 kWh/kg of COD[15]. Coca et al[16] studied efficiency of ozonation and effect of various operating parameters when it was used for decolorization of beet molasses fermentation wastewater. Performance of Fenton oxidation process was tested for decolorization of biologically treated effluent of baker's yeast industry[17]. Mane et al[18] studied application of chemically treated bagasse for treatment of distillery wastewater. A hybrid nanofiltration(NF) and reverse osmosis(RO) pilot plant was used to remove colour of the distillery wastewater[19].

These options were tried either on diluted and synthetic wastewater or they are energy and cost intensive. Coagulation is a very effective method of decolourisation and removal of solids from the wastewater. There are numerous references available in literature about use of common coagulants for industrial wastewater treatment. This paper addresses the pre-treatment in the form of cost effective option of coagulation of anaerobically digested molasses spentwash(ADMS) so that biological treatment can be given to it without any dilution.

2. Materials and Methods

2.1. Wastewater

The study has been carried out on actual wastewater collected from a nearby 30 KLD distillery, producing rectified spirit using sugarcane molasses as raw material. Anaerobically digested molasses spentwash(ADMS) was collected from the overflow of the anaerobic digester and was brought to the CESE, IIT Bombay and was stored at 4°C in cold room till experimentation.

2.2. Colour Measurement

Intensity of colour was measured in terms of absorbance at 475 nm. Samples were diluted in 1 M phosphate buffer to maintain pH of 7. Samples were centrifuged at 10,000 rpm for 10 minutes prior to absorbance determination, for eliminating hindrance due to suspended particulates in the sample. After that, the supernatant was diluted 100 times and the absorbance was measured using Thermo Spectronic visible spectrophotometer(Model Helios Epsilon, USA). Reduction in colour was estimated in terms of reduction in absorbance with reference to that of the control(original ADMS).

2.3. COD

COD was measured by closed reflux method using HACH COD digester(Model DRB 200, USA) as given in Standard Methods(APHA-AWWA-WEF, 2005). Samples were suitably diluted with distilled water.

2.4. Other Parameters

Tests for other parameters were carried out as per Standard Methods[20] for characterization of the ADMS and treated ADMS samples.

2.5. Coagulation Studies

In the present study, commonly available coagulants viz. ferrous sulphate, ferric sulphate, ferric chloride, calcium chloride, calcium oxide, calcium hydroxide, alum, potash alum and poly aluminium chloride were examined for their efficiency of decolourisation and COD reduction. To simulate field conditions, all the coagulants used were of laboratory grade, procured from local market.

Jar tests were performed on undiluted ADMS samples with coagulants. VELP Scientifica jar test apparatus(Model JLT6, France) was used. Six one litre samples were taken in six one litre beakers and flash mixed at 100 rpm for 2 minutes followed by slow mixing at 20 rpm for 30 minutes. After appropriate settling time varying from 1 to 8 hours, the supernatant samples were drawn for further analysis. First, the optimum pH was found on the basis of reduction in absorbance in the pH range 2 to 12. Lime or HCl was used for pH correction. At optimum pH, optimum dose was found out by varying dose of coagulant over a wide range.

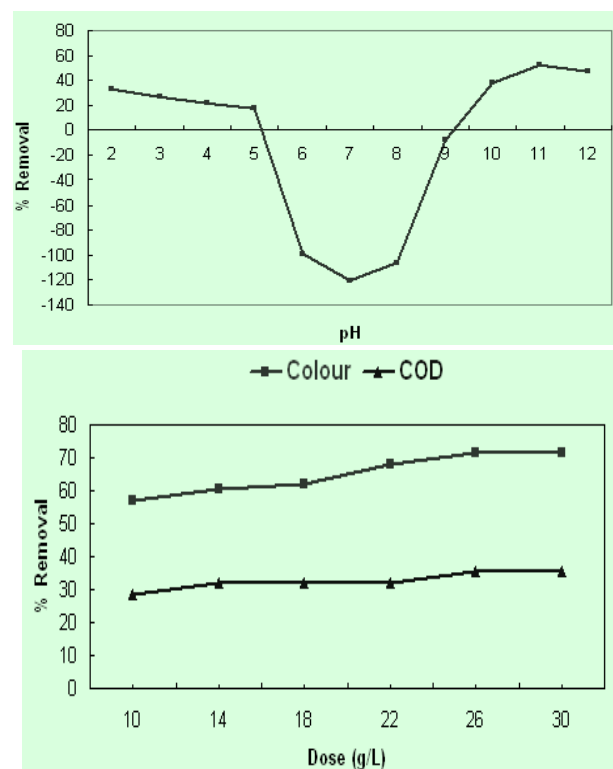


Figure 1. Colour Removal by Coagulation with Ferrous Sulfate

3. Results and Discussion

Results of pH and dose optimization for various coagulants and spectra of 100 times diluted ADMS and coagulant treated ADMS are shown in following sections.

The optimum pH for ferrous sulfate was 11 and its dose of 26 g/L gave reduction of 71% in colour and 36% in COD (Figure 1). Ferric chloride (Figure 2) is effective coagulant, widely reported in literature as this gives Fe^{3+} ions. Ferric chloride worked best at pH of 4, giving 50% colour and 39% COD removal at 8 g/L. Figure 3 shows optimum pH for ferric sulfate which was also 4 and addition of 8 g/L could achieve 43% reduction in colour with 28% reduction in COD. However, both the ferric salts were found to impart greenish colour to the treated sample. Even at smaller doses, although absorbance at standard wavelength (475 nm) was reduced but overall colour of the spentwash was worse than control.

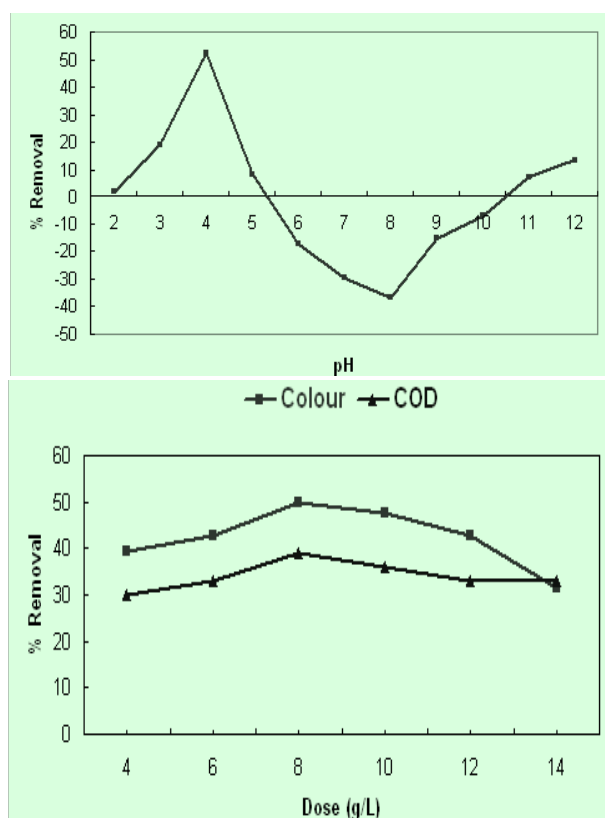


Figure 2. Colour and COD Removal by Coagulation with Ferric Chloride

At the optimum pH of 10 for calcium hydroxide, 46% reduction in colour with 32% reduction in COD was noticed at a dose of 14 g/L (Figure 4). The settling property of sludge was very poor with the volume of sludge generated being about 30% of total volume after 8 hours of settling. Calcium chloride when tested for its optimum pH, to work as coagulant, showed different trend as compared to calcium hydroxide (Figure 5). The performance of calcium chloride was the best at pH of 12 and colour and COD reductions were 49% and 21%, respectively at 18 g/L. In case of calcium oxide, optimum pH found was 11. At about neutral pH (5 to 8), there was increase in the absorbance of the

ADMS (up to 48% at pH of 6). Maximum removal of 48% colour and 28% COD could be achieved with addition of 18 g/L of calcium oxide (Figure 6).

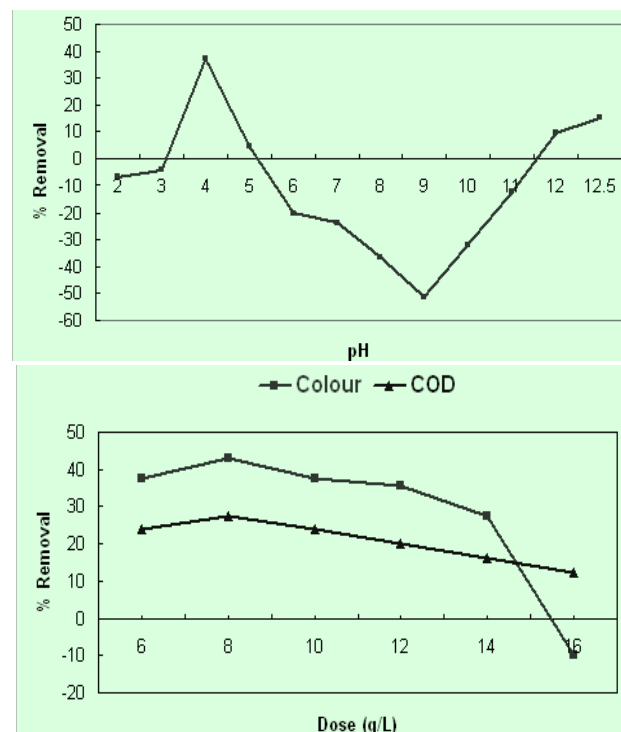


Figure 3. Colour and COD Removal by Coagulation with Ferric Sulfate

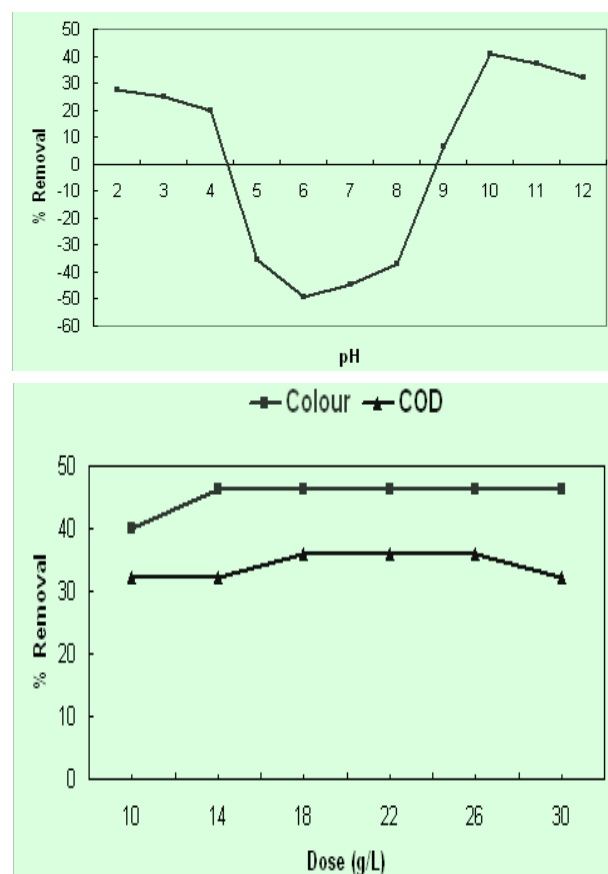


Figure 4. Colour and COD Removal by Coagulation with Calcium Hydroxide

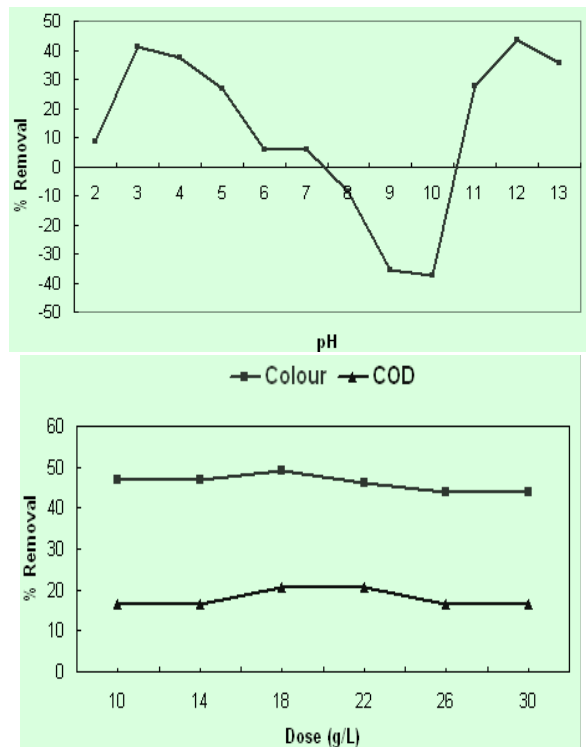


Figure 5. Colour and COD Removals by Coagulation with Calcium Chloride

Based on colour and COD removal performance, ferrous sulphate and alum were selected for double coagulation study in combination with lime.

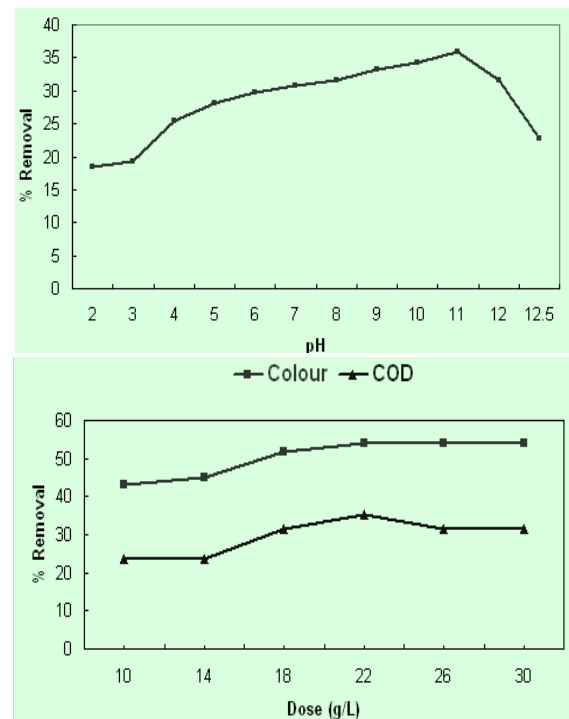


Figure 7. Colour and COD Removal by Coagulation with Potash Alum

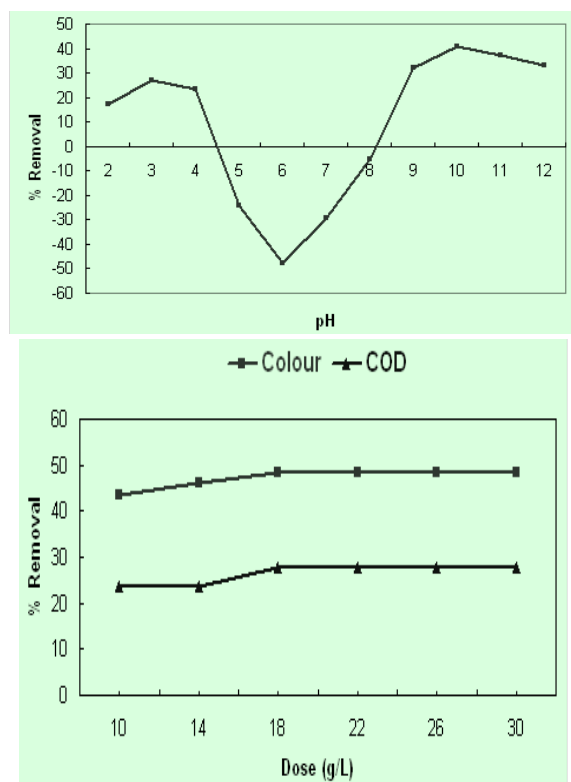


Figure 6. Colour Removal by Coagulation with Calcium Oxide

Potash alum (Figure 7) performed the best at the pH of 10. Maximum colour and COD reductions of 54% and 35% were seen at 22 g/L. Figure 8 shows that optimum pH for using alum as coagulant was 11. When Alum was used, 61% and 31% reductions in colour and COD were achieved.

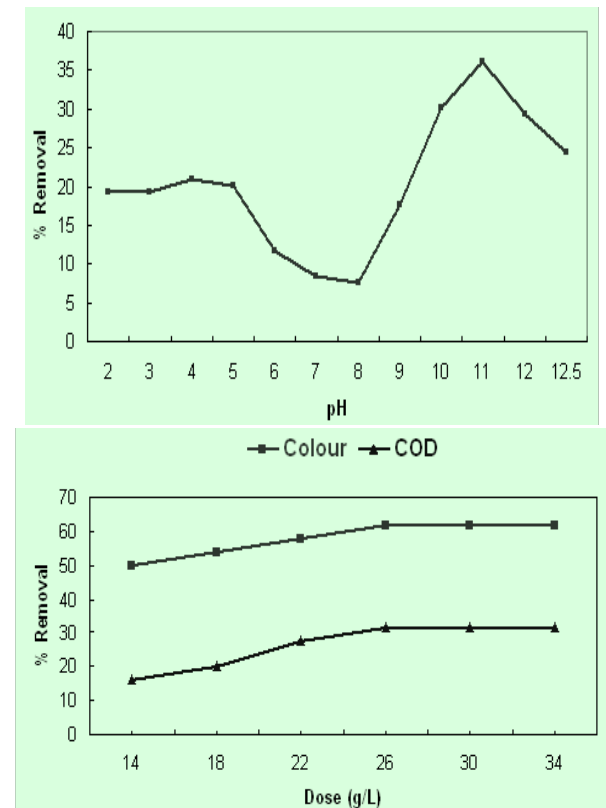


Figure 8. Colour and COD Removal by Coagulation with Alum

Commercially available coagulant poly aluminium chloride (PAC), which is reported to be very effective as well as economical for various industrial wastewaters, was also

tried in this study. Poly aluminium chloride(PAC) worked at its best at the pH as 6(Figure 9). PAC removed 63% colour and 50% COD from the ADMS at dose of 8 g/L. A cationic flocculent-aid, *Mahafloc*, manufactured by M/s Ami chemicals, Vadodara was tried for assessing possibility of reducing dose of the PAC. The flocculent-aid could not reduce the total dose of the coagulant but the settling property of sludge improved and consequently total volume of sludge generated was reduced to about 20% as compared to about 30% without using flocculent-aid.

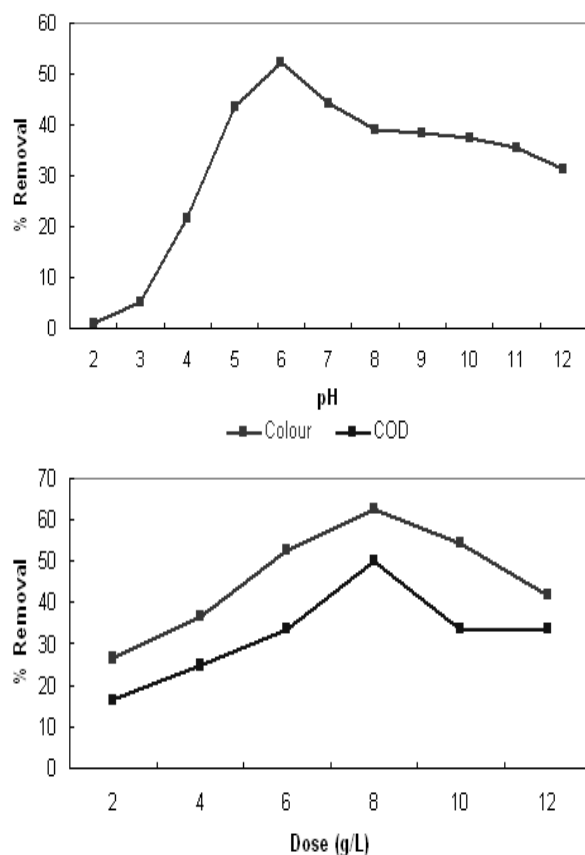


Figure 9. Colour and COD Removal by Coagulation with PAC

After single coagulation with ferrous sulphate, pH of ADMS dropped to 8.55, which was adjusted to 11 by adding lime. At second stage coagulation, overall reduction in 83% in colour and 46% in COD was attained(Figure 10). The overall dose requirement was 40 g/L. The limitations of this option were again the same as those for lime, *viz.* high coagulant dose; excess sludge formation and high retention time due to poor sludge settling. At the first stage, sludge volume was found to be about 70% of the sample after 10 hrs settling and 50% after 10 hrs settling in the second stage. Hence, double coagulation can not be recommended as feasible pre-treatment option.

Single coagulation by alum gave about 60% reduction in colour with corresponding 30% reduction in COD at 26 g/L, however, the pH of the treated sample dropped to 7.55 after the coagulation. Again pH was increased to the optimum i.e. 11 and optimization of dose was done as shown in Figure 11.

At second stage, addition of 22 g/L of alum gave overall

reduction of 75% in colour and 39% in COD(Figure 11). Despite good results of removal, double coagulation could not emerge as pre-treatment option. Very high dose requirement *viz.* 48 g/L renders the process uneconomical and other limitation of the double coagulation was the formation of excess sludge(about 60% of sample volume at first stage and about 50% at the second stage), hence, throughput was insignificant. Double coagulation with alum gave overall 75% colour and 39% COD removals at overall dose of 48 g/L. High coagulant dose; excess sludge formation and high retention time due to poor sludge settling were found to be the limitations of the double coagulation. Hence, double coagulation could not be recommended as feasible pre-treatment option. Moreover, coagulation with ferric salts was dropped as they imparted greenish colour and coagulation with calcium salts was eliminated as the sludge produced showed extremely poor settling characteristics.

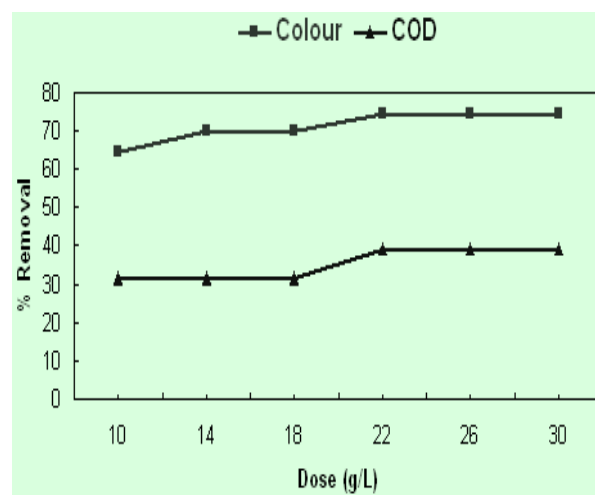


Figure 10. Colour and COD Removals at Different Doses of Alum at Second Stage in Double Coagulation

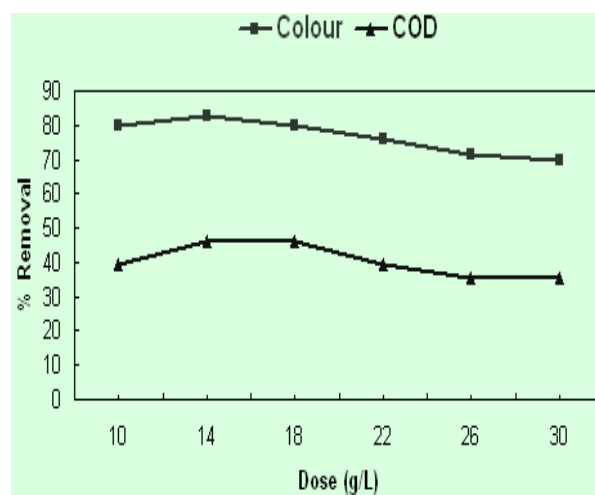


Figure 11. Colour and COD Removals at Different Doses of Ferrous Sulfate at Second Stage in Double Coagulation

Cost analysis of coagulation study shows that all the options are economically viable(with cost of treatment ranging between Rs. 0.052-0.458/L; 1\$=Rs.50). Table 1 presents summary of coagulation study along with their economics.

Table 1. Summary of Coagulation Study

S. No.	Coagulant	Optimum pH	pH Adjusted by	Dose for pH Correction	Dose of Coagulant (g/L)	% Reduction		Cost of Treatment(Rs./L)		
						Color	COD	For pH Correction	For Coagulation	Total
1	Ferrous Sulfate	11	Lime	15 g/L	26	71.4	35.7	0.030	0.169	0.199
2	Ferric Chloride	4	HCl	18 mL/L	8	49.8	39.0	0.090	0.264	0.354
3	Ferric Sulfate	4	HCl	18 mL/L	8	43.0	27.6	0.090	0.368	0.458
4	Calcium Hydroxide	10	Lime	12 g/L	14	46.4	32.1	0.024	0.028	0.052
5	Calcium Chloride	12	Lime	18 g/L	18	49.2	20.8	0.036	0.234	0.270
6	Calcium Oxide	10	Lime	12 g/L	18	48.4	27.6	0.024	0.180	0.204
7	Potash Alum	11	Lime	15 g/L	22	54.1	35.2	0.030	0.176	0.206
8	Alum	11	Lime	15 g/L	26	61.5	31.4	0.030	0.195	0.225
9	Poly Aluminium Chloride	6	HCl	5 mL/L	8	62.5	50.0	0.025	0.200	0.225
10	Double Coagulation by Alum	11	Lime	25 g/L	48	74.6	39.0	0.050	0.360	0.410
11	Double Coagulation by Ferrous Sulfate	11	Lime	22 g/L	40	82.5	46.4	0.044	0.260	0.304

5. Conclusions

Coagulation of anaerobically digested molasses spentwash(ADMS) with poly aluminium chloride(PAC) was very promising pre-treatment option which not only removed organic loading and colour of the ADMS considerably but made it suitable for biological treatment also. Further studies on rendering the fungal treatment to such primarily treated ADMS without any dilution are under the way and are showing promising results.

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