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Assessment Of Coagulation Process For The Distillery Spent Wash Using Alum Polyelectrolyte And Fenton

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All over the world, around 61% of distillery industries utilize sugarcane molasses to produce the ethanol and rectified spirit. Gradually demand of ethanol, alcohol and rectified spirit increases on a large scale. Ethanol rectified spirit and alcohol production in distillery industries in India is 8-15% by quantity, it illustrates that 85-92% distillery spent wash (wastewater) generated by volume. As a result, distillery industries comprise an enormous unpleasant impact on the surroundings. Numbers of clean up techniques have been worked out to competently treat the distillery spent wash (DSW). Coagulation processes were carried out using alum polyelectrolyte and advanced oxidation process, such as fenton were implemented to treat the DSW. Polyelectrolyte Magnafloc 1011, Magnafloc 1997, Zetag 63 and Zetag 7650 were implemented. Treatment with alum cum polyelectrolyte (Magnafloc 1011, 1 mg/L) gave 29% COD removal at pH 8. Fenton reduces maximum of COD to 79%. Maximum decolourization achieved was 98% by application of hydrogen peroxide dose in the ratio of 4:1 at 45°C. At higher peroxide dose, the effect of temperature on COD removal efficiency is very small.

KEYWORDS

Distillery spent wash, Electrocoagulation, Biomethanation

1. INTRODUCTION

Indian distilleries produce 27, 00,000 m^3 rectified spirit and generating nearly 4,05,00,000 m^3 spent wash per annum (15-20 L/L of alcohol). The population equivalent of distillery spent wash based on BOD_5 is 6.2 billion. Thus the involvement of distilleries in India to organic pollution is around six times the current population of India [1]. Other effluents generated from distillery industries consists of yeast sludge, cooling water, boiler blowdown, bottling plant waste, floor washings and other miscellaneous sources, like leakages and spillages [2]. Distillery spent wash causes a serious threat to water quality in numerous states of the country - lowering of pH value of the tributary, higher organic load (BOD, COD), etc.

Depletion of dissolved oxygen content, destruction of aquatic life and bad smell are some of the major pollution problems. Groundwater contamination by effluent with high BOD and salt content near the lagoon sites in most of the distilleries has been widely reported [3]. Ministry of Environment and Forests (GOI) has specified minimal national standards for different industries taking into account the characteristics of effluents based on which effluents should have pH between 5.5-9, suspended solids of 20 mg/L and a maximum BOD level of 15 mg/L prior to disposal. It also states that all efforts supposed to be made to eliminate colour and objectionable odour as far as feasible. In some cases, pollution law allows BOD upto the limit of 500 mg/L (terrestrial disposal). Appropriately designed and controlled treatment system has to be accepted for disposal purpose, taking into account soil and crop characteristics [4,5]. There is numerous treatment techniques are available for handling distillery spent wash, which includes aerobic, anaerobic, physico-chemical, etc. Each of these technologies has different levels of acceptability and techno-economic feasibility based on characteristic merits and demerits [6]. The quality of spent wash after anaerobic treatment will not be adequate to meet the discharge requirements and requires additional treatment. Some distilleries have adopted secondary aeration process capable of reducing 90-95% of BOD. However, the secondary treated effluent will still contain appreciable levels of COD and colour, which will pose serious problems of disposal.

Since the COD/BOD ratio following primary and secondary treatment increases from 2.5 to 20, biological

Table 1. *Experimental condition*

Initial pH	Alum (mg/L)	Polyelectrolyte (1 ppm)
8	5000	Magnafloc 1011
		Magnafloc 1997
		Zetag 63
		Zetag 7650
10		Magnafloc 1011
		Magnafloc 1997
		Zetag 63
		Zetag 7650
11		Magnafloc 1011
		Magnafloc 1997
		Zetag 63
		Zetag 7650
Experimental conditions for Fenton treatment are pH 3.2, time 4hr, COD 4637 – 4789 mg/L, H_2O_2: COD ratio (0.5:1; 1:1; 2:1; 3:1; 4:1)		

treatment may not be effective in further removal of organics. Coagulation/flocculation is a very effective method for removal of colour and suspended matter present in wastewater. Common coagulants, like lime, alum, ferric chloride and ferrous sulphate are generally recommended for industrial wastewater treatment [7]. Oldham had achieved 90% colour removal from a Kraft mill effluent having an initial colour concentration of 2285 Pt-Co units with a lower lime dosage (500 mg/L) and by using magnesium (Mg^{++} = 60 mg/L) [8]. Augustine elaborated that fenton reagent enhances the biodegradability of distillery spent wash alongwith reduced toxicity, lower COD and colour removal [9]. Fenton oxidation process optimizes at pH 3 and optimal dose of Fe^{2+} and H_2O_2 was 0.1 g and 1 mL/100 mL ADSW. It was observed that the fenton process depends heavily on factors, such as pH of the solution, the amount of both hydrogen peroxide and $FeSO_4$ added [10,11,12]. Hence advanced oxidation process has been implemented as an alternative source to treat the complex cumbersome distillery spent wash.

2. MATERIAL AND METHOD

The feed spent wash used in this research work represents actual samples obtained from full-scale anaerobic treatment plants at Padmshri Dr. Vitthalrao Vikhe Patil Distillery Industry, Loni district, Ahmednagar, Maharashtra. Initial pH of the sample is 8, COD is 14336 mg/L. Sample dilution was carried out at 1:2 and quantity is 500 mL. Lime purity (CaO%): 67, (MF) Magnafloc 1011, Magnafloc 1997, Zetag 63 and Zetag 7650 were implemented as a polyelectrolyte. Various doses of fenton reagent hydrogen peroxide (H_2O_2) were used to treat distillery spent wash.

Coagulation experiments were conducted to treat post anaerobic distillery spent wash using alum, polyelectrolytes and fenton. A dosage (5000 mg/L) of alum was added to 500 mL spent wash in a standard jar test apparatus. Different polyelectrolytes (such as Magnafloc 1011, Magnafloc 1997, Zetag 63 and Zetag 7650) were added at a dosage of 1 mg/L. The contents were mixed at 100 rpm for 5 min of rapid mixing followed by 30 min of slow mixing at 20 rpm to enhance the floc formation. After 60 min settling has been done the supernatant samples were analyzed for pH, COD and colour. The investigational conditions selected for alum and polyelectrolyte runs are summarized in table 1.

3. RESULT AND DISCUSSION

3.1 Effect of pH during alum treatment

Experiments were conducted with alum dosage of 5000 mg/L at pH levels of 8, 10 and 11. The alum dosage 5000 mg/L was selected based on preliminary trial runs. The initial COD concentration of spent wash samples used in these run were 5607, 5183 and 5031 mg/L for the three sets of trial. In each series of the run, four different polyelectrolytes (Magnafloc 1011, Magnafloc 1997, Zetag 63 and Zetag 7650) were used as coagulant aids (dosage – 1 mg/L) to assess improvements in the effluent quality and sludge settling characteristics. The experimental result shows average COD removal efficiency of 27, 14 and 12% at a pH level of 8, 10 and 11, respectively after 30 min. The result shows that the COD removal efficiency was rather low in all these runs and further indicated a decreasing trend with an increase in pH. Alum addition leads to a small decrease in pH of the medium in all the cases, caused by the acidic nature of the former. The results also show higher COD removal (27%) at pH 8. The experimental observations also do not show any significant effect of the nature of the polyelectrolyte used, at all pH levels. Magnafloc 1011, which gave better floc formation, was used for coagulation /flocculation treatment.

3.2 Fenton treatment

Experiments were conducted for 4 hr at different peroxide dosage levels (H_2O_2: COD = 0.5:1, 1:1, 2:1, 3:1 and 4:1) with initial pH 3.2 at 29°C and the result of these runs are presented graphically in terms of COD and colour removal efficiencies. The results indicate that the COD removal efficiency increases with peroxide dosage level. The maximum COD removal of 40,

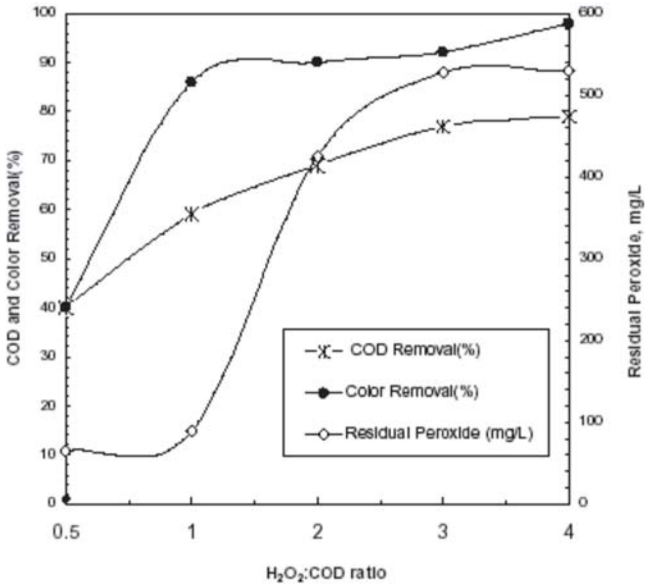

Figure 1. *Profiles of COD, colour removal (%) and residual peroxide vs H_2O_2 : COD ratio*

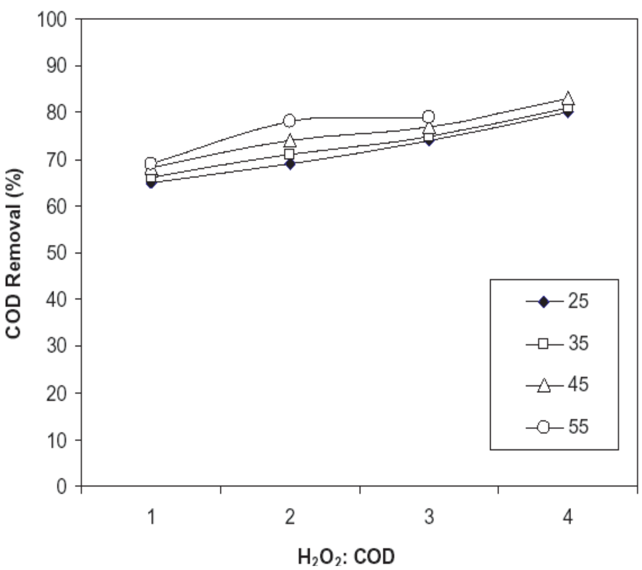

Figure 2. *Effect of temperature on COD removal efficiency during fenton oxidation at different peroxide dosage*

59, 69, 77 and 79% was obtained with H_2O_2: COD ratio of 0.5:1, 1:1, 2:1, 3:1 and 4:1, respectively. Figure 1 gives the profiles of COD removal efficiency observed at different peroxide levels. The COD removal efficiency of 77% is observed with peroxide dosage of 3:1 that improves only marginally to 79% with 4:1 peroxide dosage at the end of 4 hr reaction. A similar trend of an increase in efficiency of colour removal was observed with an increase in peroxide addition. The highest colour elimination efficiency of 40, 87, 88, 92 and 98% were examined for the dosages of 0.5:1, 1:1, 2:1, 3:1 and 4:1, respectively. The efficiency of colour removal observed is always greater than the removal of COD during fenton oxidation, which is caused by an easy transformation of the chromophoric groups. The typical profiles of peroxide dosage vs COD and colour removal efficiencies and the concentration of residual peroxide are shown in figure 1. It can be seen that the residual peroxide concentration increases rapidly with an increased peroxide dosage above H_2O_2: COD ratio of 1.0. The residual peroxide concentration increases from 90 to 528 mg/L, when the peroxide dosage was increased from 1:1 to 3:1 to yield COD removal efficiency of 59% and 77% in 4 hr reaction time. This implies a six fold higher concentration of residual peroxide (90 to 528 mg/L) in treated distillery spent wash, suggesting partial recycle in a full-scale plant to conserve peroxide.

3.3 Effect of temperature

The experimental observations in figure 2 illustrate the influence of temperature and reaction time on the efficiencies of COD and colour removal. The significant trend observed in these run is the effect of temperature, the effect of reaction period on COD and decolourization. Figure 2 gives experimental data of several runs conducted to determine the effect of temperature (25-55°C) on fenton oxidation of distillery spent wash at 25°C, 35°C and 55°C were conducted for a period upto 4 hr using H_2O_2 : COD and H_2O_2 : Fe^{2+} ratios of (1:1 to 4:1) and 50:1, respectively. COD removal of 65% was observed at 25°C increased to 68% at 35°C, with no further increase (69%) at 55°C. A higher peroxide dosage (H_2O_2 : COD = 2:1) can give COD removal of 69, 71 and 74% at 25, 35 and 45°C, respectively and a maximum of 81% was observed at 55°C. The effect of temperature on COD removal efficiency is very small at higher peroxide dosage (H_2O_2 : COD = 4:1) levels. It can also be observed that a marginal colour removal of (1-2%) for temperature 25-35°C reaction has occurred. There was no increase in colour removal efficiency with a further increase in temperature to 55°C. There was no specific effect of reaction period for COD and colour removal at the different temperatures after 1 hr reaction. The maximum COD and colour removals were observed within an hour with only a marginal removal of (1-2%) in the next 2-3 hr.

Additional experiments were conducted to assess the effect of temperature and shorter reaction period on COD and colour removal efficiency of spent wash. Figure 3 presents the effect of time on fenton oxidation at various temperature and peroxide dosages levels. COD removal of 37% observed at 25°C increased to

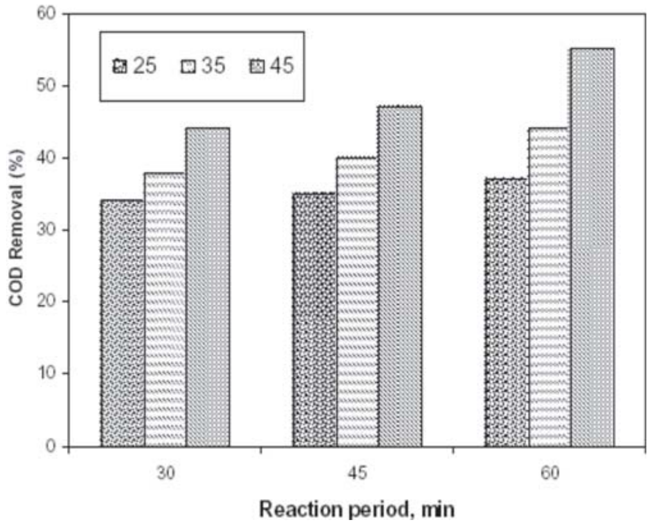

Figure 3. Effect *of reaction period on COD removal at different temperature (H_2O_2 : COD = 0.5:1)*

44% and 55% at 35°C and 45°C, respectively. A higher COD removal efficiency of 61, 63 and 66% was observed at 25, 35 and 45°C. The results shows, an increase in COD removal (33 - 37%), (35 - 44%) and (40 - 55%) achieved with 10 and 60 min reaction at 25, 35 and 45°C. Similarly, at higher peroxide dosage (1:1) COD removal of (35 - 61%), (48 - 63%) and (62 - 66%) was observed at 10 and 60 min with 25, 35 and 45°C. The bar chart shows an increase in COD removal efficiency with increase in time upto 60 min at different temperature 25–45°C and the following observations can be made during the Fenton treatment. COD and colour removal efficiencies of 79% and 98% can be achieved in 4 hr with H_2O_2: COD = 4:1 and H_2O_2: Fe^{2+} = 50:1 at 29°C, respectively. Peroxide dosage of 0.5:1 and 1:1 gave COD and colour removal efficiency of 40% and 45% and 62% and 88% at 45°C. The reaction period of 1 hr is adequate in all the runs and only a marginal increase was observed in COD (2-4%) and colour removal efficiency for the additional period upto 4 hr. Maximum COD and colour removal efficiency of 83% and 98% was observed with peroxide ratio of 4:1 at 45°C and 60 min reaction.

4. CONCLUSION

Treatment with alum (5000 mg/L) and polyelectrolyte (Magnafloc 1011, 1 mg/L) gave 29% COD removal at pH 8 (at higher pH the removal efficiency decreases). Sludge generated using Magnafloc 1011 was compact in nature as compared to other polyelectrolytes. Fenton reagent H_2O_2: COD = 1:1 to 4:1 (w/w) ratio, H_2O_2: Fe^{2+} = 50:1 and temperature (25-55°C) gave an overall COD and colour removal of 83% and 98%, respectively in 1 hr. Two fold increase in H_2O_2: COD dosage (0.5:1 to 1:1) gave 1.5 fold increases in COD removal efficiency (40-59%), whereas 3-4 fold increase in H_2O_2: COD dosage gave only 1.75 fold increase in COD removal efficiency (69%) indicating that the efficiency was not proportional to peroxide dosage in 4 hr reaction period at 29°C. Fenton trials conducted at 25-45°C, COD concentration 4336 mg/L, H_2O_2: COD ratio 0.5:1 and H_2O_2: Fe^{2+} ratio 50:1 showed COD removal efficiency is increased by 18% (37-55%) with an increase in temperature from 25-45°C. The colour removal efficiency also increases by 10% (56-66%). Fenton is advanced oxidation process which can degrade the COD and colour of distillery spent wash.

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