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Decolourization and removal of chemical oxygen demand (COD) with energy recovery: Treatment of biodigester effluent of a molasses-based alcohol distillery using inorganic coagulants

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Abstract

The removal of molasses-derived colour and chemical oxygen demand from the biodigester effluent of a molasses-based alcohol distillery effluent treatment plant was studied using inorganic coagulants—$FeCl_3$, $AlCl_3$ and polyaluminium chloride (PAC). The coagulation/flocculation yield about 55, 60 and 72% COD reductions and about 83, 86 and 92% colour reductions, with the use of 60 mM/l $AlCl_3$, 60 mM/l $FeCl_3$ and 30 ml/l of polyaluminium chloride, respectively, at their optimum initial pH. The critical pH of the effluent–coagulant mixture plays a very significant role in the coagulation/flocculation process, with pH_0 5.5 being the optimum for PAC. The solid residue, obtained by filtration and drying from the use of PAC has specific energy of 13.4 MJ/kg and can be used as a medium energy fuel material. The filtration characteristics of the flocculated effluent are poor. High COD reduction of the waste water by flocculation with PAC may be a better alternative to the conventional aerobic treatment process of the biodigester effluent.

Keywords: Distillery biodigester effluent; Chemical oxygen demand; Colour reduction; Energy recovery; Filtration; Flocculation; Polyaluminium chloride

1. Introduction

The molasses obtained from a sugar cane-based sugar mill is a prized waste as it is the main raw material to manufacture ethyl alcohol using fermentation process. The molasses contains a very high amount of reduced sugar which cannot be recovered in crystalline form, and is therefore, a waste. The recent decision of the Government of India to have mandatory use of 5% ethanol-blended gasoline for automobiles has spurred a momentum to enhance the capacity of the alcohol production in the country so as to meet the requirement of the petroleum oil refineries. The current alcohol production capacity of 2.19 million m^3 per year is slated to grow at the rate of 5% per year in India. Since the fermentation broth contains 5–12% (v/v) of alcohol, the distillation column bottoms, which is the waste water, contains 88–95% of the total volume distilled. In India, the sugar cane molasses-based alcohol distilleries generate 12–17 m^3 waste water/m^3 ethyl alcohol produced. This waste water is commonly known as distillery waste water (DWW), distillery spent wash (DSW). The distillery spent wash is dark brown in colour and has very high chemical oxygen demand (COD = 60–200 kg/m^3) and biochemical oxygen demand (BOD = 50–75 kg/m^3). The dark brown colour is imparted by the pigment called "melanoidin" which is refractory in nature to the biological treatment. Most of the distilleries in India use anaerobic biological treatment, generally upflow anaerobic sludge blanket (UASB) reactor and its variants, to recover the maximum amount of energy in the form of methane rich gas, resulting in 80–90% BOD removal and about 70% COD removal. The effluent from such reactors, generally referred to as biodigestors, thus contains very high COD (∼30–45 kg/m^3) and very high BOD (∼4.5–7 kg/m^3) depending upon their digestion efficiency [1,2]. The high COD and BOD of the distillery spent wash and biodigester effluent (BDE) are due to the presence of a number of organic compounds, such as, polysaccharides, reduced sugars, lignin, proteins, melanoidin, waxes, etc. The waste water from the biogas digester (biodigester effluent) is further treated aerobically to reduce its COD and BOD. How-

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Nomenclature

A	filtration area (m^2)
BDE	biodigester effluent
BOD	biochemical oxygen demand (kg/m^3)
c	concentration of slurry (kg/m^3)
CCC	critical concentration of flocculants
COD	chemical oxygen demand (kg/m^3)
$(COD)_0$	initial concentration of biodigester effluent
DWW	distillery waste water
k_p	slope for the plot of Eq. (1) (s/m^6)
Δp	pressure drop across the filter (Pa)
pH_0	initial pH
R_m	filter medium resistance (m^{-1})
t	time (s)
V	cumulative average volume of filtrate collected (m^3)

Greek symbols

α	average cake resistance (m/kg)
β	intercept for the plot of Eq. (1) (s/m^3)
μ	viscosity of the filtrate (Pa s)

ever, the final effluent still has high COD (8–15 kg/m^3) and BOD (1–2 kg/m^3). Since the regulatory agencies in India have notified discharge water quality standards for release into surface waters (BOD < 0.03 kg/m^3, COD < 0.01 kg/m^3) and sewers (BOD < 0.10 kg/m^3, COD < 0.30 kg/m^3), the treated effluent is diluted manifold by mixing with raw water extracted either from surface water sources or ground aquifers. This dilution, although permitted by the regulating agencies, is a matter of great environmental concern, as it does not reduce the absolute pollution load of the effluent. Further, it pollutes a large amount of fresh raw water used for dilution. Thus, a comprehensive treatment strategy for the distillery biodigester effluent so as to meet the discharge quality standards for distilleries is still lacking. The dark brown colour of the BDE due to the presence of malanoidin is another cause of concern, since the colour interferes with the absorption of sunlight and, therefore, reduces the natural process of photochemical reactions for self-purification of the surface waters. Therefore, the decolourization and the removal of COD from the BDE acquires immense importance from the environmental point of view.

Various treatment methods like wet oxidation (WO), thermolysis followed by WO and chemical coagulation/flocculation have been attempted for the treatment of BDE. Severe operating conditions (temperature 150–250 °C and pressure 0.3–20 MPa) and high capital cost limit the application of the WO process. A few studies have attempted to reduce the severity of the WO [3,4]. Catalytic thermolysis of the BDE at 140 °C and autogenous pressure, in the presence of CuO catalyst, has proved its efficacy in reducing the COD by about 70% and BOD by about 83%, with substantial (∼48%) energy recovery in terms of solid residue [3]. A three-step treatment process for BDE having thermal treatment followed by flocculation with an anionic polyelectrolyte and WO has also been suggested [4]. An inorganic polymer of ferrihydroxysulphate $[(Fe_2(OH)_9(SO_4)_{(3-n)/2}]$ has been used as a flocculant for colour removal of DSW and molasses wastewater [5]. Garg [6] has used a number of inorganic salts which act as coagulants/catalysts and flocculate at ambient temperature, for the removal of dissolved solids and colour of black liquor from pulp and paper mills. Iron and aluminium salts [7] have also been used for the coagulation and precipitation of dissolved colour and COD from a mechanical pulping effluent.

Srivastava et al. [8] have shown the potential of polyaluminium chloride (PAC) 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_0) of 3 and PAC dosage of 3 g/l, about 80% COD removal and 90% colour removal could be obtained. PAC, which has multivalent aluminium cations present in it, has shown best performance as compared to other coagulants in terms of removal of colour, turbidity, etc.

The present paper aims to study the use of different coagulants, such as, $FeCl_3$, $AlCl_3$ and PAC for the removal of colour and COD from the biodigester effluent of a sugar cane-based alcohol distillery. The effect of pH_0 and the coagulant dose has also been studied on the removal of colour and COD. From operational point of view, the filterability of the flocculated mixture is very important. Therefore, the gravity filtration studies have also been conducted to understand the filtration characteristics. The resulting solid residue and the filtrate have been analysed for C, H, N, S and ash content. The residual concentration of aluminium and iron in the filtrate and the residue has also been evaluated.

2. Materials and methods

2.1. Materials

The biodigester effluent was obtained from Sir Sadi Lal Chemicals and Distillery Ltd., Mansoorpur, U.P. (India). The analysis of the effluent is shown in Table 1. Analytical reagent (AR) grade chemicals have been used for the analysis of the parameters during coagulation/flocculation studies. Laboratory reagent (LR) grade $FeCl_3·6H_2O$ and $AlCl_3$ obtained from s.d. Fine Chemicals Ltd., Mumbai (India), and the commercial grade aqueous solution of polyaluminium chloride were used in the experiments. The characteristics of the PAC, $AlCl_3$ and $FeCl_3·6H_2O$ are given in Table 2. The X-ray diffraction pattern of the solid PAC sample supplied by another company was performed earlier by Srivastava et al. [8]. The major components identified were $AlCl_3$, Al_2O_3, Al_2SiO_5 and $3Al_2O_3·2SiO_2$. The scanning electron micrographs of the PAC at 100× and 1000× magnification showed small particulate structure in a matrix and also the larger porous particles embedded into it [8].

2.2. Experimental method

0.20 dm^3 of BDE was taken in a 0.50 dm^3 glass beaker. The pH of the effluent was noted and the initial pH (pH_0) was adjusted by adding aqueous NaOH (1 M) or H_2SO_4 (1 M) solu-