Biophysical Approach - As an Economic Treatment Method for the Colour Reduction of Biomethanated Molasses Spent Wash

Monica Shukla 1, Vivek Srivastava 2, Ajay Kumar 3

1, 2, 3 Department of Biotechnology, Faculty of Engineering and Technology, Rama University Kanpur, Uttar Pradesh, India

Abstract: The distillery effluent generated by alcohol industries is highly acidic (pH 3.8 - 4.4) with high rates of BOD & COD values and thus causing extensive contamination of environment. The present study was conducted to find out the economic pollution reduction technique for colour removal of anaerobically treated spent wash using natural decolourizing agents by performing experiments in batch and continuous mode. The different process parameters like operation condition, contact time and spent wash concentrations were analysed during the batch experiments. Maximum decolourization was obtained for 10 % v/v spent wash concentration with 1 gm soil and 0.5 gm bagasse under shaking condition. Fixed bed column study was carried out to optimize flow rate, residence time and spent wash concentration for decolourization. Maximum colour reduction in continuous mode experiments was found to be 88% for 30 % v/v effluent concentration at flow rate 1.0 ml/min using soil and bagasse combination.

Keywords: Adsorption, BOD, COD, Melanoidin, Decolourization, Bagasse, Soil, Flyash

I. INTRODUCTION

Alcohol fermenting industries are among the most polluting industries in the world as it generates huge amount of effluent discharge. In India, there are around 295 distilleries with a total installed capacity of 3198 million liters per annum and yearly production of 1587 million liters alcohols [1]. This waste water discharge has become a global concern and is one of the major causes for land and water pollution. Water is the most essential need for survival; hence fresh and clean water is the basic necessity for every living organism but rapid industrialization and indiscriminate discharge of untreated or partially treated effluent has imposed the several severe adverse effects on environment as it contains many potentially hazardous chemicals. Thus, the treatment of distillery effluent to permissible concentration is essential before its discharge.

Molasses is mainly used as a raw material for the alcohol production in India. After fermentation by yeast, alcohol is recovered by distillation and spent wash- a dark brown coloured liquid, with acidic pH (2.5- 4) remains behind [2] (Figure1) which is around 80% of the raw material to the environment. [3-4]. Its dark brown colour is due to the presence of brown polymers called melanoidins which are formed by the Maillard amino carbonyl reaction [5]. It is very difficult to treat the colour as it is hardly degraded by the conventional treatments (dilution, biomethanation, amendments with soil, etc) and can even be increased during anaerobic treatments, due to repolymerization of non biodegradable recalcitrant compounds [6-7]. Apart from the colour, distillery spent wash has also high COD, BOD, suspended solids, inorganic solids [8]. The biochemical oxygen demand (BOD) and chemical oxygen demand (COD), the index of its polluting character, typically range between 35,000–50,000 and 100,000–150,000 mg/l, respectively [9]. It has the elemental concentration of total N: 21,000 ppm, P: 4,000 ppm, K: 20,000 ppm, Ca: 32,000 ppm, Mg: 18,000 ppm and Na: 14,000 ppm [10].

Excessive amounts of Spent Wash discharged into receiving waters are dangerous and may pose a serious threat to aquatic ecosystem. The odour of spent wash spread over the area and result into serious public hazard [11]. Due to this, the management of effluent is a necessary for the distillery industries in sake of environmental pollution.
Several treatment methods have been explored for reducing the organic content of molasses spent wash. In biological methods, anaerobic treatment is an accepted practice for treatment of spent wash but however even after treated by anaerobically; the pollutant level cannot meet effluent standards laid by CPCB [13]. Bio-methanation followed by aerobic treatment used as primary treatment step in majority of the Indian distillery units. During this process, effluent is allowed for anaerobic digestion for removing the organic load and thus produced biogas is used as fuel to generate steam for fermentation process [14-15]. This process is followed by aeration, composting, concentration and incineration methods but it requires high capital cost. Moreover, the concentration and incineration process also carries drawbacks of clogging and clumping, either during evaporation or in incineration, due to presence of potassium. Many authors have reported physico-chemical methods like coagulation and flocculation, oxidation, ultrafiltration, sonication etc. for treatment, but these methods require high reagent dosages and generate large amount of sludge and thus cannot be employed in industries. Further to this, Indian distillery industries have been told to achieve zero discharge of spent wash by charter of Central Pollution Control Board. Through this study we are aiming that biomethanated distillery spent wash could be treated using cost effective carriers through packed bed column. The system would work on the biophysical approach to remove colour. The spent carrier material system would ensure the improvement of soil quality and would enhance agriculture crop yield. Also we are achieving zero discharge and good return of investments and would be able to achieve the parameters of permissible limits of treated effluent set by Ministry of Environment and forest (MOEF) and Central Pollution Control Board (CPCB).

II. MATERIALS AND METHODS

A. Sample Collection
The molasses spent wash (MSW) after biomethanation was collected from Unnao Distilleries and Breweries Limited located near Kanpur city (Uttar Pradesh), India. The optical density of different concentrations of MSW was determined on UV-visible spectrophotometer at wave length of 475 nm (λmax of Melanoidin).

B. Batch Mode Experimental protocol
To investigate the extent of decolourization using soil and bagasse, batch test were carried out for 10-50% concentration of molasses spent wash under agitation and static condition by withdrawing the samples at regular interval. The experiment was carried out by adding 1 gm dried and sieved soil and 0.5 gm bagasse as absorbent in 10ml of spent wash samples ranging from 10-50% v/v dilution in 50 ml capacity conical flask. Contents were agitated using rotary shaker at 150 rpm for 15 mins and then filtered through
whatman filter paper no. 1. The filtrate was allowed for centrifugation at 12000rpm for 12 mins. Decolourization was observed using UV-Visible Spectrophotometer at 475nm ($\lambda_{\text{max}}$ of Melanoidin). The percentage of colour degradation is measured by:

$$\text{% colour degradation} = \frac{[\text{C}_i - \text{C}_f] \times 100}{\text{C}_i}$$

Where, $\text{C}_i$ and $\text{C}_f$ are the initial absorbance and final absorbance of the spent wash [16-17].

A plot was drawn to determine the maximal colour reduction for a spent wash dilution.

C. Experimental Design for Continuous Reactor Setup
Five laboratory scale Fed Batch Reactors having 30cm height and 7 cm in diameter were setup for the treatment of the molasses spent wash effluent. Adsorption bed used in the experiment contained soil, bagasse and flyash in different combination to check the maximal efficiency of carrier materials for decolourisation. Three of the reactors are packed with soil and bagasse in ratio of 100:70, 100:100 and 70:100 and rest two reactors have combination of soil, bagasse and flyash in ratio of 100:70:100 and 100:70:70 (Figure 2) to yield the desired bed height. Biomethanated molasses spent wash of different dilutions 10-50%v/v, were passed through the column at constant flow rate in different batches. The treated effluents were collected at the outlet of the column once the steady state was achieved and absorbance was measured by UV-Visible spectrophotometer at 475nm using 50X diluted samples. The different parameters like bed shrinkage, residence time and flow rate were also monitored.

![Fig 2: Schematic Diagram of Laboratory Scale Packed Bed Reactor](image)

III. RESULTS AND DISCUSSION
The aim of the study was to attain the maximal colour reduction from distillery molasses spent wash using cost optimized and eco friendly method using bagasse and soil. The recalcitrant nature of melanoidin and high organic load of effluent makes difficult to treat spent wash with conventional treatment processes. Hence, Biosorption of heavy metals and other organic pollutants have been studied by many scientists [18-21] and can be considered as economic technology for colour removal.

A. Batch Studies
The experiment was carried out by treating the different strength (10-50%v/v) of molasses spent wash with soil and bagasse combinations under both shaking and static condition. Maximum colour removal was found in 10 % spent wash concentration with 1 gm soil and 0.5 gm baggase. Decolourization up to 48% was achieved for 50% diluted spent wash (Figure 3).
The effect of contact time on decolourization was studied under static condition for effluent concentration ranging from 10-50% v/v (Figure 4- Figure 8). Maximum colour reduction of 84.56% was achieved for 40% MSW dilution.
Fig. 6: Decolourization pattern of 30% Molasses spent wash at different contact time

Fig. 7: Decolourization pattern of 40% Molasses spent wash at different contact time

Fig. 8: Decolourization pattern of 50% Molasses spent wash at different contact time
B. Packed Bed Reactor Studies

The results obtained from batch experiments were used to study the extent of discolouration of MSW using packed bed column. The different combinations of decolourizing agents and effluent flow rates were optimised and it was found that the maximum decolourization of 88% was achieved for soil and bagasse in ratio of 70:100 at input flow rate 1.0 ml/min (Figure 9, 10) and residence time of 51 hrs. It was observed that better performance was achieved at lower flow rate [22]. The decrease in extent of decolourization at higher flow rate would be due to insufficient residence time of effluent. The residence time of the solute inside the column is an important parameter in designing of a packed bed column.

Therefore, it can be concluded from the present study that, the combination of soil and bagasse which is byproduct of sugar industry, may be used as efficient, natural and cost effective alternative for the treatment of distillery molasses spent wash.

![Decolourization results of spent wash after PBR treatment](image)

**Fig. 9:** Decolourization results of spent wash after PBR treatment

![Decolourization pattern obtained from column run using soil and bagasse](image)

**Fig. 10:** Decolourization pattern obtained from column run using soil and bagasse
The study highlighted the combined efficiency of soil and bagasse, as natural decolourizing agents for the removal of melanoidin from molasses spent wash. At 40% effluent concentration, maximum decolourisation was observed under static condition. Further, packed bed column operations were performed and decolourisation of 88% was achieved at flow rate 1.0 ml/min. The other parameters, bed shrinkage 7.8% and residence time of 51 hours were observed. The results revealed that soil and bagasse could be used as for the successful removal of colour from distillery spent wash.

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REFERENCES


