Flyash Adsorption Studies for Organic Matter Removal Accompanying Increase in Dissolved Oxygen

Sunil J. Kulkarni, Suhas V Patil, and Y. P. Bhalerao

***Abstract*—In the present scenario of indian economy, sugar mills and distilleries are backbone of agro-industrial economy.At the same time these industries are facing severe effluent treatment problems.They treat effluent by conventional methods which are not adequate In the present work attempt is made to remove organic matter from the effluent by using bagasse flyash as an economical adsorbent. The studies were carried out in a batch operation to optimize the parameters like adsorbent dose, pH, initial concentration and contact time. The dissolved oxygen of the diluted effluent (1% concentration) was also reported along with COD. Experimental results for 100 ml of batch sample indicates that with an increase in adsorbent dose, COD decreases steeply up to 3 gm, and remains constant with further increase in adsorbent dose. Moreover, the dissolved oxygen of a diluted effluent (1% concentration) was found to increase from 3 mg/l to 8.5 mg/l. This analysis shows the importance of increased dissolved oxygen content for the aquatic life. The optimum pH, contact time and initial concentrations were found to be 6, 2.5 hr and 6000 mg/l respectively.**

***Index Terms*—Batch adsorption, flyash, Chemical Oxygen demand, dissolved oxygen**

I. Introduction

In todays world distilleries have their own succesful contribution to countris economy.Ethyl alcohol, the major product of distilleries is going to be very valuable because of rising fuel prices. Among the raw material sources for distillery, two very important raw materials are cane sugar molasses and beet sugar molasses. Distillery waste water (stillage) is the main by product originating in the distilleries, and its volume is 10 times of ethanol produced.. It is not surprising that the utilization of the stillage raises serious problems, and that many attempts have been made all over the world to solve them.

Distillery wastewater is usually comprised of high volume of greatly acidic matter which presents many disposal and treatment problems. Waste streams generally contain high levels of both dissolved organic and inorganic materials.

The treatment of the effluent for removal of organic matter can be carried out by various chemical and biological methods. Still there is potential for adoption as an important method for it. Activated carbon adsorption can be considered as one alternative. But 10-20 % loss during regeneration is a limitation to this method considering huge size of effluent treatment plants and the quantity of the effluent. The limit for disposing off the effluent to the river and inland water is 250 mg/l. The DO of the effluent ranges from zero to 4 for the distillery effluent.

The adsorption operation exploits the ability of certain solid to preferentially concentrate specific substance from solution onto their surfaces. In this manner, the component of either gases or liquid solutions can be separated from each other. The scale of operations range from the use of a few grams of adsorbents in the laboratory to industrial plants with an adsorbent inventory exceeding 35000 kg The adsorption is effective method for removal of inorganic and organic pollutants from effluent of various process industries.

Adoptation of bagasse flyash, a sugar industry solid waste into zeolitic material for the uptake of phenol was studied by Shah *et al.* [1]. Ahamaruzzaman [2] has studied Role of flyash in removal of organic pollutants from wastewater. Removal of dissolved organic matter by granular-activated carbon adsorption as a pretreatment to reverse osmosis of membrane bioreactor effluents was studied by Reznik *et. al.*[3]. Marin and. Beiras [4] have carried out work on adsorption of different types of dissolved organic matter to marine phytoplankton .

Matilainen *et al.* [5] presented coagulation and flocculation as effective methods for removal of natural harmful organic matter from water. Ren *et. al.*[6] experimentally reported the application of carbon nanotubes (CNTs) as a new type of adsorbents for the removal of various inorganic and organic pollutants, and radionuclides from large volumes of wastewater.

Hami *et al.* [7] investigated effective use of powdered activated carbon (PAC) on the performance of a pilot-scale laboratory dissolved air flotation (DAF) unit. Experimental findings shows that for dosages of activated carbon in the range of 50–150 mg/l, the removal efficiencies for BOD increased from 27–70% to 76–94% while those for COD increased from 16–64% to 72–92.5% for inlet values of 45–95 mg/l and 110–200 mg/l for BOD and COD respectively.

Alvarez *et al.* [8] reported the application of a

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simultaneous combination of ozone and granular activated carbon as a tertiary treatment of a wastewater generated from the activity of various food-processing industries. Chaudhari *et al.*[9] carried out experimental investigations on the removal of molasses-derived color and chemical oxygen demand from the biodigester effluent of a molasses-based alcohol distillery effluent treatment plant using inorganic coagulants. Flocculation with carbon was found to be a better alternative to the conventional aerobic treatment process of the biodigester effluent.

Mohana *et al.* [10] presented an overview of the pollution problems caused by distillery spent wash, the technologies employed globally for its treatment and its alternative use in various biotechnological sectors. Satyawali and Balakrishnan [11] presented a review of the existing status and advances in biological and physico-chemical methods.

Adsorption is a low cost and important physical process for the treatment and renovation of wastewater. Activated carbon is a highly effective low cost adsorbent and shows 10 –15 % carbon loss during regeneration. Reader and Miller [12] studied the effect of estimations of ultraviolet absorption spectra of chromophoric dissolved organic matter on the uncertainty of photochemical production calculations.

Hyung and Kim [13] have used natural organic matter for adsorption to multi-walled carbon nanotubes and also observed the effect of natural organic matter characteristics and water quality parameters. COD is the amount of oxygen consumed for oxidizing the organic matter. In the present study the oxidizing agent used is potassium dichromate.

The minimum requirement of DO content for the aquatic life is 5 mg/l. The dissolved oxygen is very significant characteristic of the effluent. The effluent containing very low DO is harmful for aquatic life because it affects adversely the DO of the reservoir or river in which it is disposed. The maximum DO that water can have is called saturation DO which is 9.1 at 20 ^{o}C. The DO is inversely proportional to temperature. The factors affecting the dissolved oxygen are: reareation, deoxygenating, respiration and photosynthesis [14, 15]. If the DO of the water is less than saturation DO then the mass transfer of atmospheric oxygen into the water takes place. A deoxygenation is mainly due to utilization of dissolved oxygen by the organic matter in the wastewater. Respiration is the oxygen consumption by fishes and other aquatic life. Photosynthesis is carried out by the plant in the process of utiling food to synthesize energy. In this process oxygen is evolved. [16].

Oxygen consumption values can be used to quantify the amount of organic matter present in the wastewater. The typical COD and BOD of the distillery effluent are 70000-100000 and 45000-60000 respectively. By using primary and secondary treatment it can be brought down to 5000 – 8000. For further removal of organic matter many advanced methods have been tried. The UASB reactor for post treatment of distillery waste water was reported by Musee *et. al.* [17].A Distillery spentwash was treated in the hybrid anaerobic reactor by Gupta and Singh [18].

This paper presents the experimental investigations of adsorption process for removal of organic matter using bagasse flyash from distillery effluents. The effects of various parameters like adsorbent dosages, pH, initial concentration and contact time on chemical oxygen demand and dissolved oxygen were also reported with their optimum values.

II. Experimental Work

The following parameters were optimized during the study: adsorbent dosage, pH, Contact time and initial COD. For all the above parameters 100 ml of distillery effluent was taken into 500 ml conical flasks and adsorbent was added. The flasks were kept on shaker and the samples were filtered and collected for analysis. The COD of the effluent and DO of the diluted effluent (1% concentration) were measured for each run. The dissolved oxygen was measured by using soil and water analysis kit by inserting the electrode probe into the wastewater.

For the measurement of COD, the waste water containing known amount of potassium dichromate with known normality was kept at 150^{O} C on COD digestion apparatus (spectralab-2015 M) for 2 hours. From the literature and the available data, two hours are sufficient for the organic matter to decompose.

The blank containing distilled water instead of waster water in the sample tube is also kept at same temperature and for same duration. Silver sulphate and mercuric sulphate are used to fasten the process of decomposition. After two hours the samples were cooled and titrated with Mohrs salt (Ferrous ammonium sulphate) of known concentration using ferroin indicator. The difference in the burette reading for blank and the sample is indicator of the difference in potassium dichromate concentration. The COD is estimated by calculating the equivalent concentration of organic matter required for the consumption of potassium dichromate.

III. Results and Discussion

A. Effect of Adsorbent Dosage

Fig.1 presents the variation of chemical oxygen demand and dissolved oxygen with variation in adsorption dosages. The effect of adsorbent dosage was studied by keeping the initial concentration, pH and contact time constant. It was observed that an increase in adsorbent dose favors the COD removal. This dependence becomes more insignificant at higher doses of adsorbents. This may be because of inability of the adsorbate to utilize the adsorbent, and at very high concentration all the organic matter may not have reached to the entire adsorbent surface. The optimum adsorbent dose was found to be 3 gm for 100 ml of effluent. The DO of the diluted effluent (1% concentration) increased from 3 mg/l to 8.5 mg/l, after this adsorbent dosage the corresponding DO of the diluted effluent approaches a constant value.

B. Effect of pH

Fig. 2 depicts the variation of Chemical oxygen demand and dissolved oxygen with PH. The effect of pH on the COD removal and DO diluted effluent (1% concentration) was observed by keeping other parameters constant.

Adsorption phenomenon is analogous to ion exchange process. The pH of the aqueous solution has significant effect on organic matter adsorption by the adsorbent; pH of the solution also influences the actives sites and therefore, solution chemistry. Effect of variation of pH on COD is presented in Fig. It is observed from same figure that the COD removal rate increases with increase in pH up to the value of 6 and decreases further with increase in pH .The rate of COD removal of organic matter increases with increasing pH valued from 3 to 6. Further increase in pH doesn't favor the adsorption. It is also seen from present study that % removal of organic matter observed to be maximum at corresponding pH value of 6.The dissolved oxygen content goes on increasing in between pH of 6 and 7. Further it drops to 5 at the pH of 10.

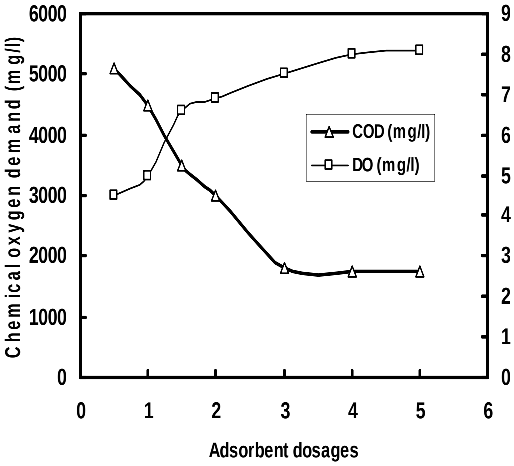

Fig.1. Effect of adsorption dosages

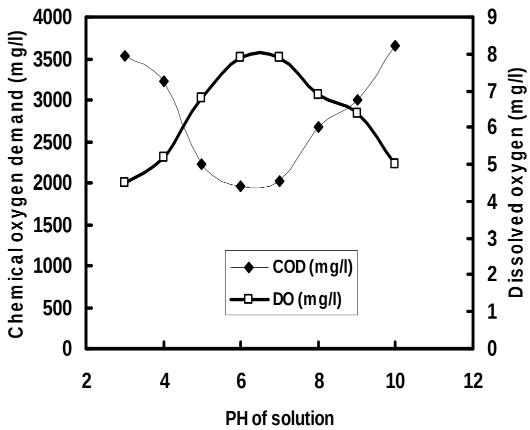

Fig 2. Effect of PH

The value of optimum DO diluted effluent (1% concentration) was observed to pH is found to be 6 to 7.

C. Effect of Contact Time

Fig. 3 indicates the variation of Chemical oxygen demand and dissolved oxygen with contact time. The effect of contact time on COD of the effluent and DO of diluted effluent (1% concentration) was studied by keeping the adsorbent dose and pH at optimum level i.e. 3 gm per 100 ml and 6 respectively. As contact time was increased the COD removal was found to increase up to 150 minutes. There after the adsorbent saturates and further increase in contact time has no effect on the COD removal. Also DO level increases from 3 mg/l to 8.5 mg/l. The optimum contact time was found to be 150 minutes.

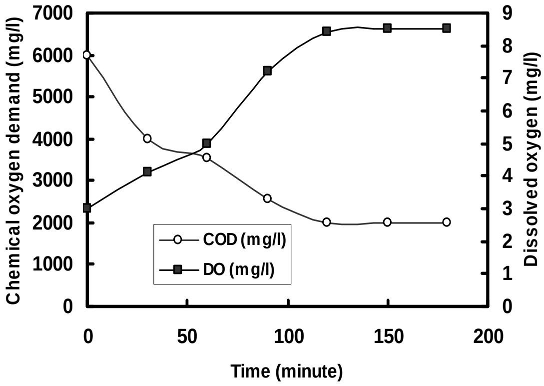

Fig. 3 Effect of contact time

D. Effect of Initial COD

Fig. 4 shows the variation of % COD removal and % DO increase with initial COD. The effect of initial COD i.e. organic matter concentration on COD removal and DO was studied. The samples of various COD concentration were obtained by diluting the effluent. The % COD removal is high at high initial COD. This is because of high concentration difference. Excessively high initial concentration is not desirable.

The optimum initial concentration depends on the capacity of the adsorbent to adsorb the adsorbate. In the present case the initial COD concentration of 6000 mg/l is found to be the optimum for the maximum COD removal of 78%. The increase in DO of diluted effluent (1% concentration) is found to be 166%, with decrease in the initial COD from 6000 mg/l to 500 mg/l, the % COD removal decreased from 78% to 25%.

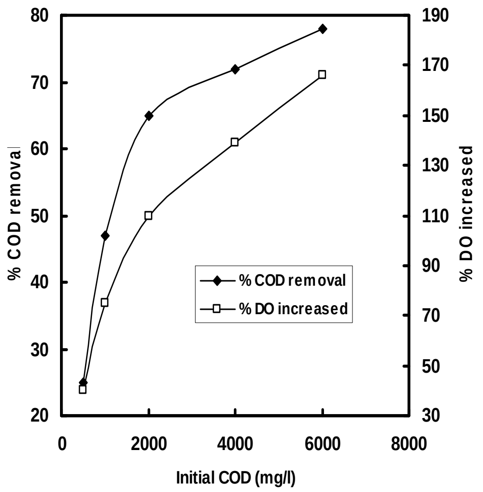

Fig.4 Effect of initial COD

E. Adsorption Isotherm

Freundlich isotherm is presented in following empirical equation -$X/M = b\, C^{*m}$

$\ln X/M = \ln b + m \ln C^*$. Here X/M is the catalyst loading , C* is the equilibrium concentration of organic matter, b and m are constants.

Fig.5 shows the equilibrium data for Freundlich isotherms. At initial concentration of 6000 mg/l the effluent was treated with different amount of adsorbents M. The equilibrium concentration C^* was determined by allowing sufficient time to attain the equilibrium concentration C*and same was plotted against X/M. The amount of adsorbate adsorbed (X), is the difference between initial concentration C_o and C^*, the equilibrium concentration.

It is observed from Fig.5 that adsorption process for present study reasonably follows the Freundlich adsorption pattern. The values of b and m are observed to be 1339.43 and 0.707 respectively.

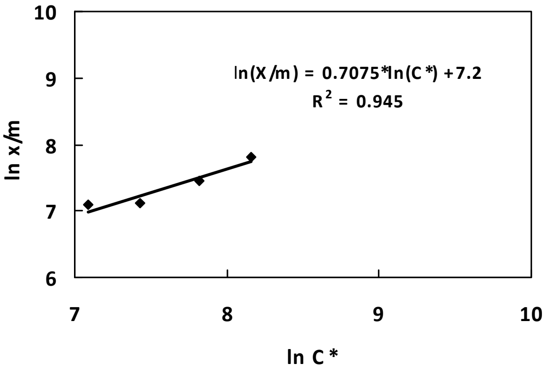

Fig. 5. Freundlich isotherms

IV.CONCLUSION

The bagasse flyash is found to be effective adsorbent. The % COD removal obtained was 78 to 85. The adsorbent dosage, pH, contact time and initial concentration of organic matter have significant effect on the COD removal and dissolved oxygen. The dissolved oxygen content of the wastewater is the indicator of its organic matter.

- Higher the COD minimum is the DO, because DO is consumed by organic matter. If COD is less then corresponding value of DO expected to be higher.
- It is also found that there is a certain limit for increasing the adsorbent doses for given amount of effluent. This has to be carefully controlled. An excess use can leads to uneconomical process. The initial concentration plays an important role throughout the adsorption. The optimum initial concentration was also reported in the present study.
- The adsorption was found to favor in acidic conditions. The data obtained from the present study is directly applicable for continuous column design in order to decide various main parameters such as height of adsorption column, initial concentration, residence time and flow rate.
- The flyash can be regenerated by thermal regeneration in multi hearth or rotary furnace in presence of steam to volatize and carbonize organic matter. Other chemical and biological methods are also available. Regeneration and disposal depends on the amount and the availability of the adsorbent.

APPENDIX

BOD	biological oxygen demand
COD	chemical oxygen demand
CNT	carbon nanotubes
DAF	dissolved air floatation
DO	dissolved oxygen
PAC	powdered activated carbon
UASB	upflow aerobic sludge blanket reactor

Symbols

C^*	equilibrium concentration
C_o	initial concentration
M	mass of adsorbent
b,m	constants
X	Amount of adsorbate adsorbed

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