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Adsorption of Methylene Blue from Aqueous Solution - A Comparative Study for Colour Removal Efficiency of Bagasse Fly Ash and Brick Kiln Ash

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Abstract: The excessive release of colour into the environment is a major concern worldwide. In this study, the use of low-cost adsorbents has been investigated as a replacement for the current conventional and often expensive methods of removing dyes from aqueous solutions. The adsorptive removal of Methylene blue dye was achieved using a packed bed column (down flow method), comparing Bagasse Fly Ash and Brick Kiln Ash as adsorbents. The effects of various factors such as influent concentration, flow rate and bed height were analysed. The column experiment showed that for the optimum influent concentration of 50 mg/l, the concentration dropped to 0.080 (99.83% reduction) and 0.097 (99.80% reduction) mg/l respectively after treatment by Bagasse Fly Ash and Brick Kiln Ash respectively. For 10cm bed height and 10ml/min flow rate, beyond 50mg/l concentration of dye, the capability for removing dye decreased. For the different bed heights, the percentage reduction increased with the increase in bed height due to the availability of more number of sorption sites. At optimum bed height (7.5cm), the percentage reduction achieved was 99.72% and 99.70% respectively. For the different flow rates, the percentage reduction decreased with the increase in flow rate because at higher flow rate, the contact time between adsorbate and adsorbent was minimized. At optimum flow rate (10ml/min.), the percentage reduction achieved was 99.62%, and 99.70%, respectively for Bagasse Fly Ash and Brick Kiln Ash. It is concluded that while Bagasse Fly Ash shows 0.03% higher efficiency than Brick Kiln Ash, this difference is too small to conclude that Bagasse Fly Ash is better than Brick Kiln Ash in terms of removing Methylene blue dye. However, Both Bagasse Fly Ash and Brick Kiln Ash can be deemed to be more effective than conventional methods. Also Freundlich isotherm was found to best fit for both of the adsorbents indicating that this study can be used for large scale treatment.

Keywords: Bagasse Fly Ash, Brick Kiln Ash, Methylene Blue, Adsorption

I. INTRODUCTION

Recent urban and rural expansion has tremendously increased the water consumption which has resulted in many fold increases in wastewater production. The wastewater is a mixture of sewage water, agricultural drainage, industrial waste effluents and hospitals facilities. It is well known that the wastewater from domestic origin contains pathogens, suspended solids, nutrients (nitrogen and phosphorus) and other organic and inorganic pollutants (Andrew et al., 1997). In order to minimize the environmental and health hazards, these pollutants need to be brought down to permissible limits for safe disposal of wastewater (Manju et al., 1998; Poots et al., 1978). Therefore, removal of the organic contaminants and pathogens from wastewater is of paramount importance for its reuse in different activities (Ali and Deo, 1992; Chen, 1997; Raj et al., 1997).

The conventional wastewater treatment technologies as adopted in industrialized nations are expensive to build, operate and maintain especially for decentralized communities (Mazumder and Roy, 2000; Piet et al., 1994; Mazumder and Kumar, 1999). Research efforts are underway for the development of treatment technologies suited to these decentralized communities (Wang et al., 2005). Fly ash can be used as a promising adsorbent for removal of various types of pollutants from wastewater (Wang and Hongwei, 2006). Low-cost adsorbents of different origin such as industrial waste material, bagasse fly ash and jute-processing waste can also be used for removal of organic matter from wastewater (Bhatnagar, 2007; Srivastava et al., 2005; Banerje and Dastidar, 2005). The COD and BOD concentrations play an important role in the re-use of these waste effluents. Adsorption-based innovative

technology developed with low-cost carbonaceous materials shows good potential, especially for COD removal from the domestic wastewater (Devi *et al.*, 2002; Devi and Dahiya, 2006).

The textile industry, from its beginnings, has been hampered by the large volumes of water required for the preparation and dyeing of cloth. More recently, waste generation has also become a considerable concern for textile manufacturers and finishers. Textile industry wastewater is characterized primarily by measurements of BOD, COD, colour, heavy metals, and total dissolved and suspended solids. Water with high BOD indicates the presence of decomposing organic matter and subsequent high bacterial counts that degrade its quality and potential uses. Colour and turbidity both cause an aesthetic and real hazard to the environment. The aesthetic value considers the discoloration of recreational streams and waterways. The real hazards caused by colour and solids in waste are dye toxicity and the ability of the colouring agents to interfere with the transmission of light through the water, thus hindering photosynthesis in aquatic plants. Heavy metals, typically chromium and copper, are very hazardous to human and aquatic life at relatively low concentrations.

There are many technologies currently available for treating wastewater from the textile industry such as biological treatments, chemical precipitation, Ultra filtration, Carbon adsorption, and oxidation with ozone.

The main drawback with these technologies is that they generally lack the broad scope treatment efficiency required to reduce all the diverse pollutants present in textile wastewater. However, when one approach does look promising in terms of efficiency of the treatment, then the capital costs or operating costs become prohibitive when applied to the large scale water needs common to this industry.

BOD (Biochemical Oxygen Demand) is the measure of the oxygen consuming capabilities of organic matter.

COD (Chemical Oxygen Demand) measures the potential overall oxygen requirements of the wastewater sample, including oxidizable components not determined in the BOD analysis.

Colour is defined as either true or apparent colour.

> **True colour** is the colour of water from which all turbidity has been removed.

> **Apparent colour** includes any colour that is due to suspended solids in the water sample.

Municipal aerobic treatment systems for treating sewage wastes, depends on biological activity, have been found to be ineffective in the removal of these dyes (Lazaridies *et al.*, 2003). There are two major technologies available for the dye removal, i.e., oxidation and adsorption. Oxidation method is possibly the best technology to totally eliminate organic carbons, but it is only effective for wastewater with very low concentration of organic compounds. Thus, dilution is necessary as a facility requirement. It is well known that adsorption is one of the most effective methods for the removal of colours, odour, oils and organic pollutants from process or waste effluents. Also, activated carbon is the most widely used adsorbent due to its excellent adsorption capability (Juang *et al.,* 2002). However, its use is often limited due to high cost, making this method unfavourable for the needs of developing countries like India.

Utilization of agriculture waste residues for the wastewater treatment at least has the following advantages:

A. There are available abundantly at no or low cost,
B. Disposal of the waste is a serious environmental concern.

This study was designed to investigate the adsorption capacity of Brick Kiln Ash and Bagasse Fly Ash with respect to different initial concentrations, different bed heights and different flow rates. Freundlich isotherm was studied for interpretation of results.

II. OBJECTIVES

To study and compare Methylene blue removal efficiencies of bagasse fly ash and brick kiln ash through adsorption batch process (Packed Column Bed).

III.   MATERIALS AND METHODS

A.   Experimental Procedure

1)   Preparation Of Basic Dye Solution: Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$. At room temperature it appears as a solid, odourless, dark green powder which yields a blue solution when dissolved in water. Therefore, it has many uses as a dye in a range of different fields, such as biology and chemistry.

[IUPAC NAME: - 3, 7-bis (Dimethylamino) - phenothiazin-5-ium chloride]
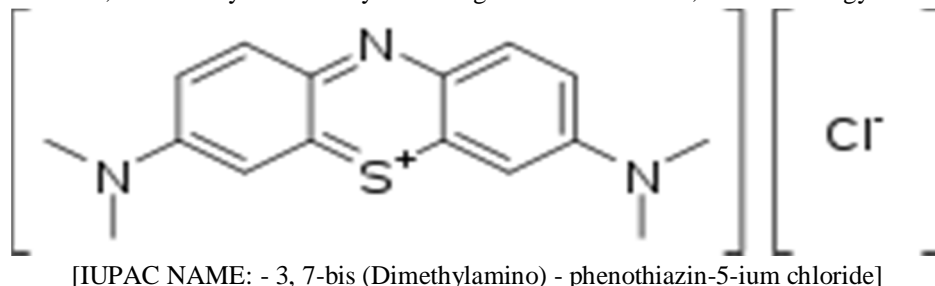
The rationale for having chosen Methylene blue for this study was that it has strong adsorption capacity onto solids. The dye is not regarded as actually toxic, but it can have various harmful effects.

Basic dye, Methylene Blue manufactured by MERCK LIMITED, was used without further purification. Methylene Blue was dried at 110°C for 2h before use. All of the Methylene Blue solution was prepared with distilled water.

The stock solution of 10 mg/l was prepared. The experimental solution was prepared by diluting the stock solution with distilled water when necessary.

2)   Fly Ash Collection And Adsorbent Development: Bagasse Fly Ash and Brick Kiln Ash samples were collected from Rajgad Sahakari sugar factory and its surrounding area respectively in Bhor, Pune. Both were oven dried at 110°C overnight and sieved through sieve No. 100 (150μ). The sieved Bagasse Fly Ash and Brick Kiln Ash were then stored in a desiccator for further use.

3)   Equipment: A Systronics UV Spectrophotometry169 was used for dye analysis. The dye concentrations were analysed at 665nm wavelength based on the specifications indicated on the Methylene Blue bottle.

4)   Column Studies: Fixed bed column studies were carried out using an acrylic column of 1.2 cm inner diameter and 40 cm length. Both samples of ash were packed in the column with two layers of glass wool at the top and bottom. The dye solution of specified concentration was charged from the top of the column in down flow method at fixed flow rate of 10ml/min for 30 minutes. The filtrate was collected and colour concentration was measured with spectrophotometer at 665nm. (P Sivakumar and P N Palanisamy, 2009) Effects of initial dye concentrations, bed heights, flow rates and weight of adsorbents were studied.

B.   Batch Adsorption Experiments

1)   Effects Of Initial Dye Concentration: Initial Methylene Blue solution concentrations of 25, 50, 75 mg/l were studied at 10 cm fixed bed height and 10 ml/min. flow rate. Then the optimum initial dye concentration was identified.

2)   Effects Of Different Bed Heights: In these experiments, initial dye concentration and flow rate were kept constant and bed heights of 5, 7.5, 10 cm were studied and then optimum bed height was identified.

3)   Effects Of Different Flow Rates: Initial dye concentration and bed height were kept constant and effects of different flow rates of 5, 10, 15 ml/min. were studied and then optimum flow rate was identified.

IV.   RESULTS AND DISCUSSION

A.   Effects Of Initial Dye Concentration

The adsorption experiments were carried out based on the conditions explained in 2.1. Figure 1 shows the percentage removal of dye as a function of initial dye concentrations at fixed bed height and flow rate. It was observed that percentage removal of dye decreases with increases in concentration from 25, 50, 75 mg/l. At higher concentration, the availability of dye molecules for the adsorption site is more, which leads to higher uptake of dye at higher concentration. (Goel J., *et al.,* 2005).

The results indicate that, for Bagasse Fly Ash and Brick Kiln Ash, the concentration of dye decreased from 50 mg/l to 0.080 (99.83%) and 0.097 (99.80%) mg/l respectively which was the optimum holding capacity of dye for both of adsorbents. After that point the capability for removing dye was decreased as the initial concentration was increased beyond the optimum concentration of 50mg/l.

B. Effects Of Different Bed Heights

The adsorption experiments were carried out based on the conditions explained in 2.2. Figure 2 shows the percentage removal of dye as a function of different bed heights at fixed dye concentration and flow rate. It was observed that the removal efficiency of dye increased with increasing bed height, implying increased adsorbent quantity, due to the availability of more number of sorption sites (i.e. the total surface area increases) (Zulfudhly Z, *et al.,* 2001) (Vijayaraghvan K, *et al.,* 2004).

The results indicate that, for Bagasse Fly Ash of initial concentration 50mg/l, the concentration of dye decreased to 0.178 (99.64%), 0.135 (99.72%), 0.094 (99.81%) for 5cm, 7.5cm, 10 cm bed height respectively and for Brick Kiln Ash (50mg/l concentration), the concentration of dye decreased to 0.193 (99.61%), 0.149 (99.70%), 0.096 (99.80%) for 5cm, 7.5cm, 10 cm bed height respectively. For both of adsorbents 7.5cm bed height was optimum.

C. Effects Of Different Flow Rates

The adsorption experiments were carried out based on the conditions explained in 2.3. Figure 3 shows the percentage removal dye as a function of different flow rates at fixed dye concentration and bed height. It was observed that rapid uptake is noticed in the initial stages and the adsorption finally reaches saturation. At higher flow rate, the contact time between adsorbate and adsorbent is minimized, leading to decreasing the removal efficiency.

The results indicate that, for Bagasse Fly Ash (50mg/l dye concentration and 7.5cm bed height), the concentration of dye decreased to 0.077 (99.84%), 0.135 (99.72%), 0.188 (99.62%), for 5, 10, 15 ml/minute flow rate respectively. For Brick Kiln Ash (50mg/l dye concentration and 7.5cm bed height), the concentration of dye decreased to 0.070 (99.85%), 0.149 (99.70%), 0.225 (99.55%), for 5, 10, 15 ml/minute flow rate respectively. For both adsorbents, 10ml/min. was optimum flow rate. The effect of flow rate is helpful for large scale treatment systems in order to utilize the bed for its maximum capacity with minimum flow rate (Aksu Z, *et al*., 2007). The extent of adsorption depends on the site of the adsorbate and other factors such as surface functional groups, types of pores present on carbon, intra particle mass transfer, etc. (Fu Y, *et al*., 2001) (Aksu Z, *et al.,* 2006).

D. Maximum Percentage Removal At Optimum Condition

Bagasse Fly Ash and Brick Kiln Ash were analysed for maximum percentage reduction with respect to optimum initial concentration (50mg/l), optimum bed height (7.5cm) and optimum flow rate (10ml/min). Figure 4 shows that Bagasse Fly Ash has marginally higher removal efficiency than Brick Kiln Ash. The difference of 0.03% is too small to effectively conclude that Bagasse Fly Ash is better than Brick Kiln Ash in terms of removing Methylene blue dye.

E. Adsorption Isotherm

The adsorption isotherm was analysed with the help of Freundlich isotherm. Freundlich model attempts to accounts for surface heterogeneity.

Freundlich isotherm: $q_e = K_f \times Ce \ (1/n)$

Where k_f is roughly measure of the adsorption capacity and 1/n is an indicator of adsorption effectiveness; q_e is the amount of dye adsorbed per unit mass of adsorbent (in mg/g) and Ce is the equilibrium concentration of dye (in mg/l). The values of Freundlich parameters were obtained from the correlation between values of q_e versus Ce. The values of R^2 for Bagasse Fly Ash and Brick Kiln Ash were found as 0.997 and 0.999 respectively showing lower variability in the data that shows this study can be applied for large scale treatment. The value of R^2 which should have in the range of $0 > R^2 > 1$ is favourable for adsorption (Walkar G.M and Weatherley L.R., 1998).

V. CONCLUSION

For influent concentration, the adsorption capacity increases with increase in influent concentration but when it reaches its saturation point, the adsorption capacity decreases with increase in influent concentration. For effects of initial dye concentration (at fixed bed height and flow rate), 50mg/l dye concentration was found to be optimum because beyond these concentration, the percentage reduction was found to decrease.

The adsorption capacity increases with increase in bed height due to the availability of more number of sorption sites. For effects of different bed height (at fixed dye concentration and flow rate), 7.5cm was found to be the optimum bed height.

The adsorption capacity decreases with increases in flow rate because at higher flow rate, the contact time between adsorbate and adsorbent is minimized, leading to decreasing the removal efficiency. For effects of different flow rate (at fixed bed height and dye concentration), 10ml/min. flow rate was found to be optimum.

The adsorption process strongly depends upon the surface area, types of pores present, intra particle mass transfer and so on.

After optimizing initial concentration of dye, bed height and flow rate, Bagasse Fly Ash and Brick Kiln Ash were analysed for maximum percentage reduction. It was found that both, Bagasse Fly Ash and Brick Kiln Ash are an effective adsorbent for the removal of Methylene Blue form aqueous solution.
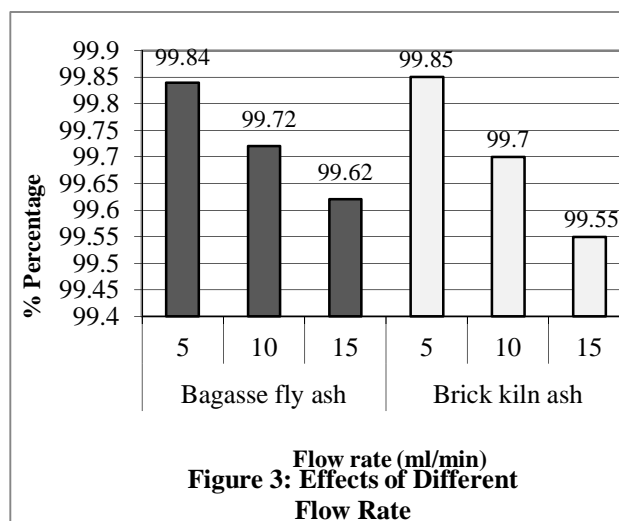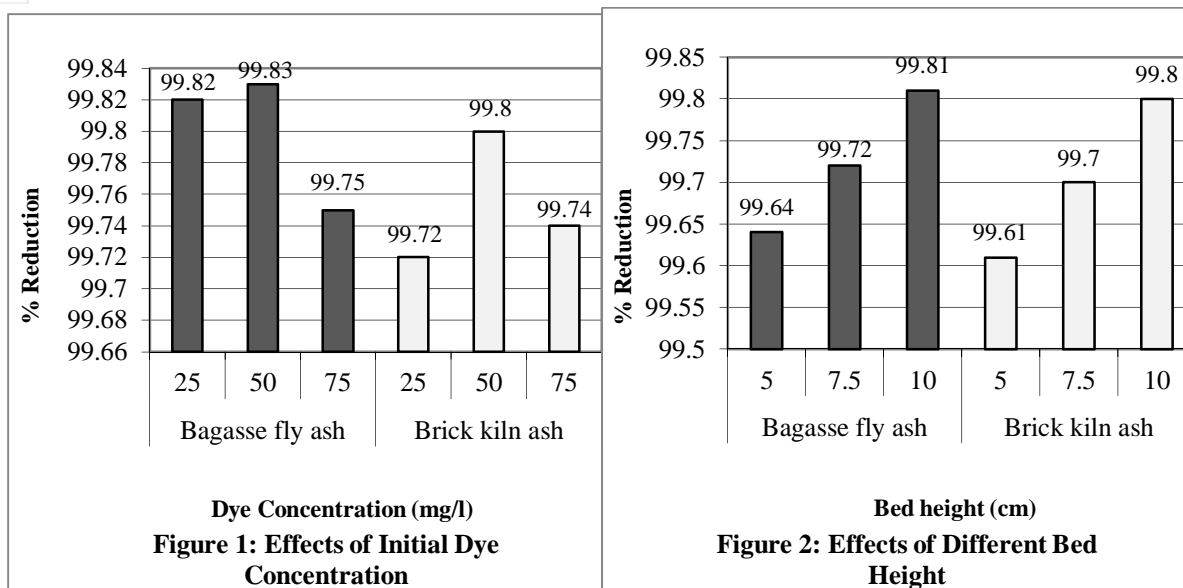
From Figure 4, it is concluded that Bagasse Fly Ash is capable of removing maximum 99.76% dye while Brick Kiln Ash is 99.73%. The effect of flow rate is helpful for large scale treatment system to utilize the bed for its maximum capacity with minimum flow rate. Freundlich isotherm was found to be best suited for the study signifying that this study can be applied for large scale treatment.

Packed bed column study having down flow method was found to have advantages over up flow method because a skilled person is not required, no electricity is required and the method is less expensive than the up flow method.
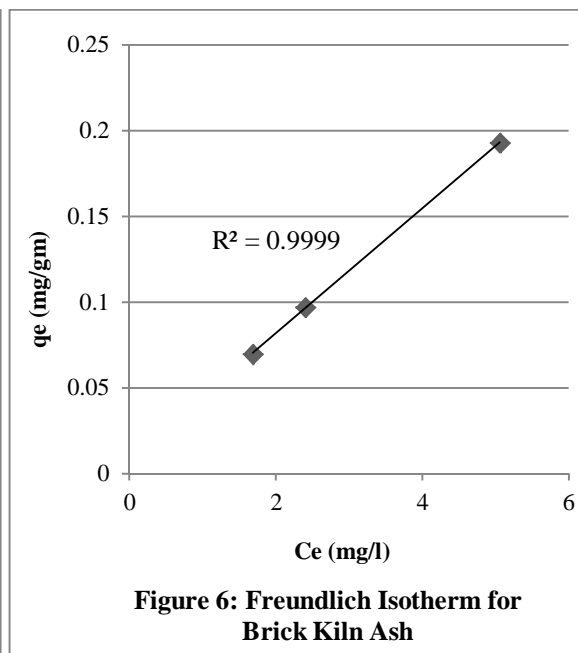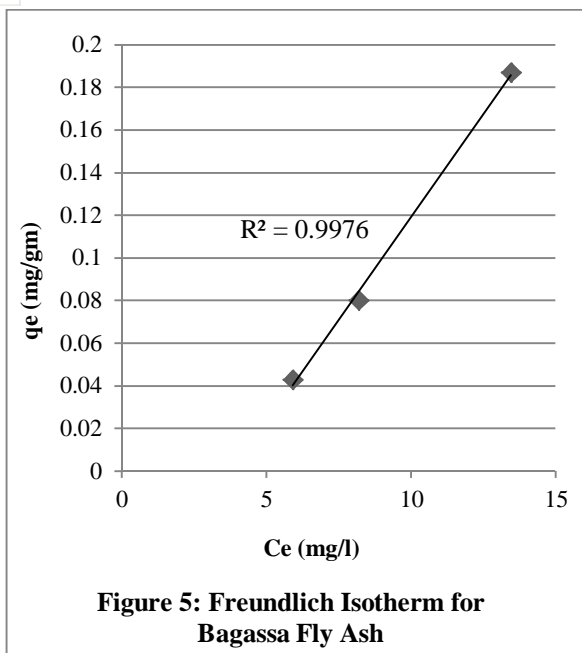
VI. ACKNOWLEDGMENT

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Figure 1: Effects of Initial Dye Concentration

Figure 2: Effects of Different Bed Height

Figure 3: Effects of Different Flow Rate

Figure 4. Maximum Percentage Reduction of Dye (at optimum condition)

Figure 5: Freundlich Isotherm for Bagassa Fly Ash

Figure 6: Freundlich Isotherm for Brick Kiln Ash

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