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COLOUR REMOVAL FROM PAPER MILL EFFLUENT USING ACTIVATED CARBON

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ABSTRACT

The Activated carbon, obtained from local paper industry, has been used as an inexpensive and effective adsorbent for the removal of colour from pulp and paper industry. Effect of various operating variables, viz., contact time, initial concentration, adsorbent dose and particle size on the removal of colour has been studied and discussed. It is found that for optimum removal of colour, contact time for adsorption equilibrium equals to 60 min., at dosage of 2 g/L of Activated carbon. The material exhibits good removal capacity (97%) and follows both the Langmuir and the Freundlich models.

INTRODUCTION

Pollution problems caused by the pulp and paper mill effluent have been one of the important environmental problems. It is among the 17 highly polluting industries in India. These mills consume large quantity of water and also discharge large volume of wastes polluting the water courses. Water requirement in paper industry is estimated to be 300- 425 m^3 ton_{-1} of paper produced (Sastry and Kamatchiammal, 1988). About 80-85% of water consumed by the industry is discharged as waste water containing organic and inorganic pollutants and colouring materials. The nature and volume of the effluent discharged varies from mill to mill and depends on the production capacity, raw material used, types of paper manufactured, pulping process, recovery of chemicals etc. It is reported that an integrated pulp and paper mill employing Kraft process generates 220-320 m^3 of effluent per ton of paper manufactured. In general small mills produce large volume of waste per ton than large mills, as they do not possess recovery units. It is estimated that about 330 m^3 of effluent is produced per ton of paper manufactured in a small mill of capacity 20 ton/day whereas 220 m^3/ton is generated in a large mill manufacturing 200 ton/day (Manivasakam 1987). Pulp and paper mill waste is a dark black colored liquid known as 'black liquor'. It has characteristically high BOD, COD, suspended solids and colour (Sastry and Kamatchiammal 1988; Dey *et al*. 1991).

Discharge of paper mill effluent into water course results in oxygen depletion, unsightly appearance and toxicity to aquatic life. The most noticeable and apparent characteristic of the effluent from such

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industries is colour. Colours not only cause the bad aesthetical effect but also reduce the self-purification capacity of rivers by inhibiting photosynthetic production of oxygen and direct destruction of aquatic communities. The colour of the pulp and paper industry varies from light brown to dark brown due to the presence of lignin and its derivatives. The effluent is normally treated by biological process such as aerated lagoon and activated sludge processes. The biological processes are very effective for removing settle able solids and stabilization of biodegradable organic fraction, but are not suitable for removing the color.

Significant work has been reported on the problem of colour removal from pulp and paper mill wastes at global level. The processes like ion flotation, chemical oxidation, ion exchange, soil percolation, electrochemical process, radiation and ultra-filtration are more of academic value (Sharma 1983; Sastry 1986; Rastogi 1995). Coagulation with alum, lime and ferric salts is one of the treatment options available for colour removal but is quite expensive and also give rise to problems due to the production of large volume of sludge. A large number of adsorbent materials, viz., activated carbon, silica, wood, saw dust, peat, fuller's earth, fly ash, etc. have also been tried for removal of pollutants (Tan *et al*. 1985; Lee and Low 1989; Cowan *et al*. 1991; Groffman *et al*. 1992; Low and Lee 1991; Kesaoul-Qukel *et al*. 1993; Rodda *et al*. 1993) but the problems of cost and handling still remain tagged with these adsorbents. Activated carbon gives very high efficiency. The present work examines the efficacy of another cheaper material, Activated carbon- a sludge waste material from paper industry, which is available in large quantities and can be used as an adsorbent for the removal of colour from pulp and paper mill effluent with appreciably lower cost, as an alternate to other adsorbents. Our earlier attempt for the removal of pollutants using this material has been quite successful (Gupta *et al.* 2002,).

METHODOLOGY

Combined effluents generated from pulp mill, bleach plant and chemical recovery sections were collected from Amlai Paper Mill, Shahdol (India), before and after treatment. The treatment process adopted in the paper mill is the activated sludge process. The raw materials used in the mill are eucalyptus, saw, hardwood, bamboo, poplar, wastepaper and wood pulp. The consumption of fresh water including domestic process and industrial cooling is 26,510 l/day. The effluent discharge including domestic waste is 23,860 l/day. The production of paper (bleached and unbleached) is 170 ton/day.

Adsorbent development

Activated carbon, a sludge waste material from paper industry, was collected from Amlai paper Mill, Shahdol (India). The material was washed with distilled water to remove dust, dirt, clay and other dissolved and undissolved solid substances and dried at 110°C. The material was then treated with Zncl2, KOH and again washed with distilled water and dried at 110°C. The dried material is sieved to obtain various fractions, <75, 75-150, 150-200, 200-250, 250-300, 300-425 µm. The material was stored in a vacuum desiccator prior to further use.

The stability of the adsorbent was determined by keeping the material overnight in different solvents (water, dilute acids and bases) and determining the presence of its constituents in these solvents. The constituents of the prepared material were determined following the standard methods of chemical analysis (Vogel 1989).

Adsorption studies

Adsorption studies were carried out in a series of Erlenmeyer flasks of 100 mL capacity covered with Teflon sheets to prevent contamination. The effect of concentration, solution, pH, adsorbent dose, and contact time and particle size were studied. A known amount of the adsorbent was added to each flask and the flasks were agitated in a water bath shaker maintained at 20°C. At prescribed time intervals, the solutions were centrifuged and the supernatants were analyzed for colour using spectrophotometer and isotherms developed.

RESULT AND DISCUSSION

Characteristics of Activated carbon

The Activated carbon was found to be stable in water, dilute acids and bases. Activated carbon is a carbonaceous adsorbent with a high internal porosity, and hence a large internal surface area. The surface area per gram of material can range from 500 to 1400 square meters, and values as high as 2500 m2/g have been reported. Active carbons are made in particulate form as powders or fine granules less than 1.0 mm in size with an average diameter between 15 and 25 mm. The composition material of the activated carbon not

only carbon element but contain with a small amount of hydrogen, nitrogen, oxygen and ash etc. Iodine number is the most fundamental parameter used to characterize activated carbon performance. Water treatment carbons have iodine numbers ranging from 600 to 1100. The density was found to be 260 gm/L.

Effect of operating variables

Equilibrium time

The effect of contact time on the removal of colour is shown in Fig. 1. The asymptotic nature of the plot indicates that there is no appreciable change in the remaining concentration after 60 min. This time is presumed to represent the equilibrium time at which an equilibrium concentration is attained. The equilibrium time was found to be independent of initial concentration. All the further experiments were, thus, conducted for 60 min. Adsorption curves are smooth and continuous leading to saturation, suggesting the possible monolayer coverage on the surface of the adsorbent. According to Weber and Morris (1963), for most adsorption processes, the uptake varies almost pro portionately with t1/2 rather than with the contact time, t. Therefore, plot of colour removed, Ct vs, t1/2, is presented in Fig. 2. The plots have same general features, initial curved portion followed by linear portion and a plateau. The initial curved portion is attributed to the bulk diffusion, the linear portion to the intraparticle diffusion and the plate to the equilibrium.

Effect of initial concentration

The effect of initial concentration on colour removal is shown in Fig. 3. It is evident from the plot that the colour removal is rapid during the initial period. Further, for the same equilibration time, the colour removal is higher for greater values of initial concentration or the percentage adsorption is more for lower concentration and decreases with increasing initial concentration. This may be due to the fact that for a fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of adsorbate thus resulting in a decrease in percentage uptake of the adsorbate corresponding to an increased initial adsorbate concentration.The maximum colour removal of about 97% is achieved in 1 h.

Effect of adsorbent dose

The effect of adsorbent dose on the removal of colour is shown in Fig. 4. It is observed that the removal of colour per unit weight of adsorbent decreases with increasing adsorbent load. On the other hand percent removal increases from 28% to 97% with increasing adsorbent load from 0.5 to 2.0 g/l. It is found that the reduction in colour increases with an increase in dose of Activated carbon up to 2 g/l and stays almost constant with further increase in adsorbent dose.

Effect of particle size

The effect of particle size of adsorbent on the removal of colour is shown in Fig. 5. It is evident from the plat that for a fixed adsorbent dose, the removal of colour is higher for smaller adsorbent size. Further, it isobserved that the percentage removal decreases with increasing geometric mean of adsorbent size. This is because, adsorption being a surface phenomenon, the smaller particle sizes offered comparatively larger surface area and hence higher adsorption occurs at equilibrium. The influence of particle size furnishes important information for achieving optimum utilization of adsorbent and on the nature of breakthrough curves for designing packed bed absorbers.

Adsorption models

In general, the adsorption isotherm describes how adsorbates will interact with adsorbents and so is critical in optimizing the use of adsorbent. Adsorption data for wide range of adsorbate concentrations are most conveniently described by adsorption models, such as the Langmuir or Freundlich isotherm, which relate adsorption density qe (uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase, Ce. The adsorption models have been used to determine the mechanistic parameters associated with the adsorption process.

Langmuir model

Langmuir's isotherm model suggests that uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm equation is represented by the followi … ir 1918):

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0 C_e}$$

Where qe is the amount adsorbed at equilibrium, Ce is the equilibrium concentration of the adsorbate

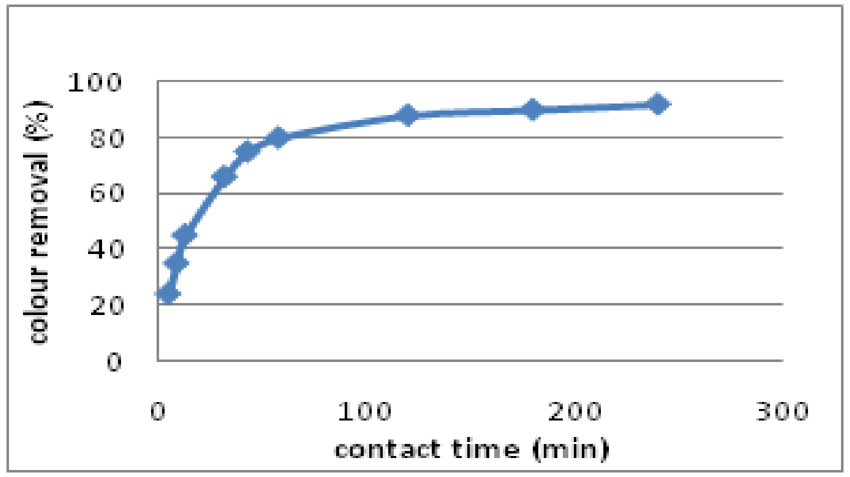

Fig. 1

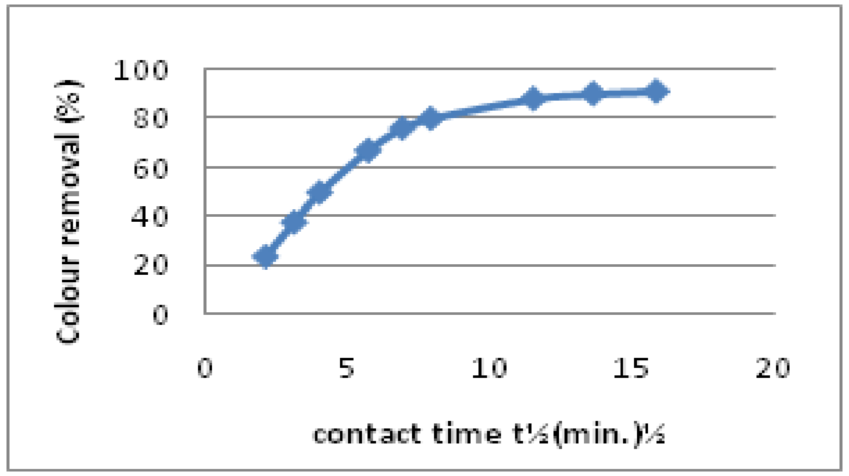

Fig. 2

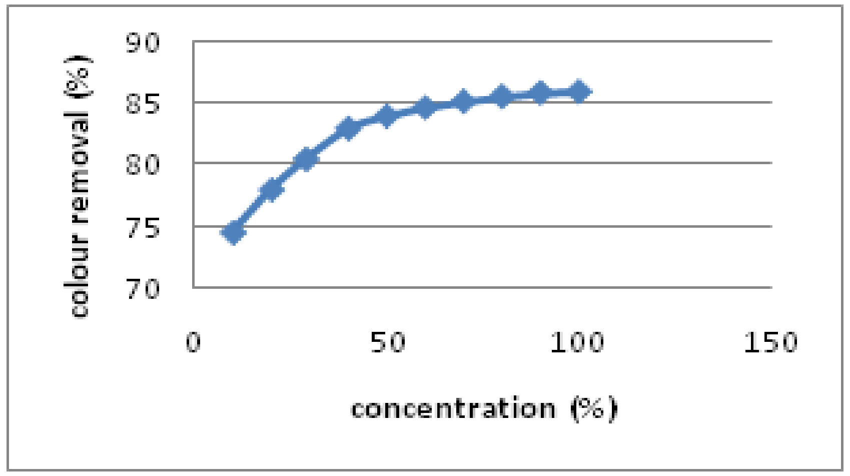

Fig. 3

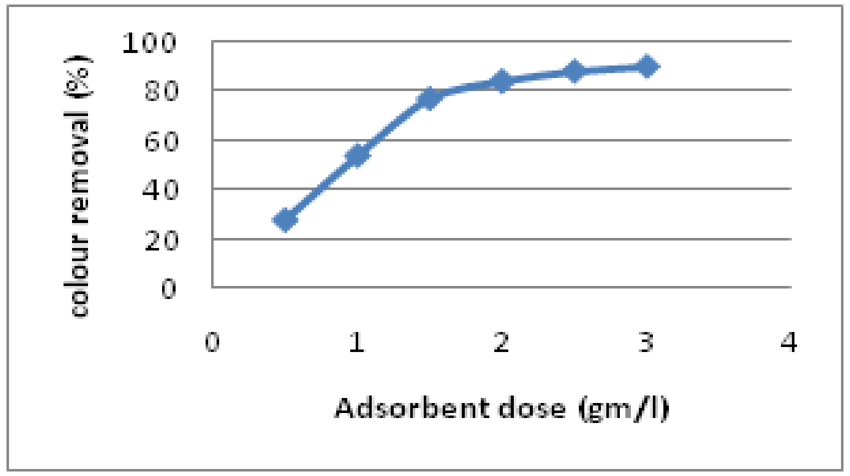

Fig. 4

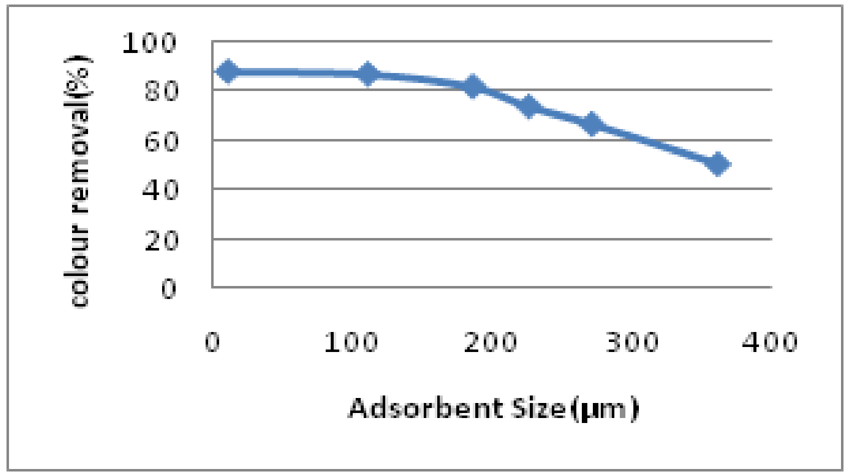

Fig. 5

ions and Q0 and b is Langmuir constants related to maximum adsorption capacity (monolayer capacity) and energy of adsorption, respectively. When 1/qe is plotted against 1/Ce, a straight line with slope 1/bQ0 and intercept 1/Q0 is obtained (Fig. 6), which shows that the adsorption follow Langmuir isotherm model. The Langmuir parameters, Q0 and b, as calculated from the slope and intercept of the plot are 88.5 and 1.71 respectively. These values may be used for comparison and correlation of the sorptive properties of the adsorbents.

Freundlich model

The Freundlich equation has been widely used and is applicable for isothermal adsorption. This is a special case for heterogeneous surface energies in which the energy term, b, in the Langmuir equation varies as a function of surface coverage, qe, strictly due to variations in heat of adsorption (Adamson 1967). The Freundlich equation has the general form (Freundlich 1926):

$$q_e = K_F C^{1/n}$$

The Freundlich equation is basically empirical but is often useful as a means for data description. Data are usually fitted to the logarithmic form of the equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Where qe is the amount adsorbed, Ce is the equilibrium concentration of the adsorbate ions and KF and n are Freundlich constants related to adsorption

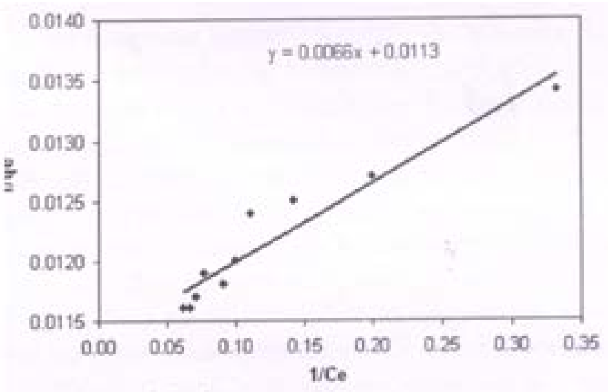

Fig. 6 Langmuir isotherm

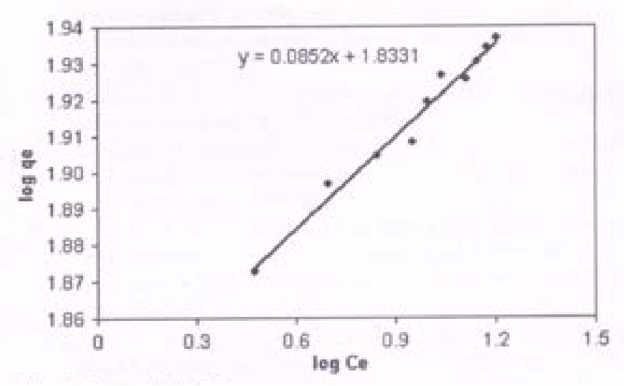

Fig. 7 Freundlich isotherm

capacity and adsorption intensity, respectively. When log qe is plotted against log Ce, a straight line with slope 1/n and intercept log KF is obtained (Fig. 7). This reflects the satisfaction of Freundlich isotherm model for the adsorption. The intercept of line, log KF, is roughly an indicator of the adsorption capacity and the slope, 1/n, is an indicator of adsorption intensity (Weber 1972). The Freundlich parameters, KF and 1/n, as calculated from the plot are 68.09 and 0.0852 respectively. It is evident from the data that the surface of the adsorbent is made up of small heterogeneous adsorption patches which are very much similar to each other in respect of adsorption phenomenon.

CONCLUSION

The present study has shown that the Activated carbon can be successfully used for the removal of colour from pulp and paper industry. The material exhibits good removal capacity and maximum removal of 97% can be achieved in 60 min. The percentage removal increases with increasing adsorbent doses, and as such removal increases with decreasing size of the adsorbent material. The equilibrium data describe both the Langmuir and the Freundlich isotherm models satisfactorily.

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