

## Adsorption of Safranin from Wastewater Using Coal Fly Ash

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**Abstract:** The discharge of highly colored effluents into natural water bodies not only is aesthetically displeasing, but also impedes light penetration, thus upsetting biological processes within stream and thus required treatment before discharge into a water body. In the present study, fly ash generated from coal based thermal powers station had been converted into a low-cost adsorbent and characterized for by SEM, EDEX, XRD and FTIR. It was used as low cost adsorbent for the removal of Safranin dye from wastewater of textile industry. Batch studies were carried out to study the effect of pH, adsorbent doses, adsorbate concentration, temperature and contact time. The results of batch studies revealed that the adsorption of Safranin was strongly pH dependent and maximum Safranin removal was observed at equilibrium pH of 9. Optimum adsorbent dose and contact time were found to be 20 g/l and 120 minutes respectively. Kinetic studies have been performed to have an idea of the mechanistic aspects and to obtain the thermodynamic parameters of the process. The results also show that adsorption decreases with increase in temperature thereby showing the process exothermic in nature. Adsorption data have also been correlated with both Langmuir and Freundlich isotherm models.

**Key words:** Fly ash, adsorption, Safranin, Langmuir, Freundlich isotherm, adsorbate, adsorbent

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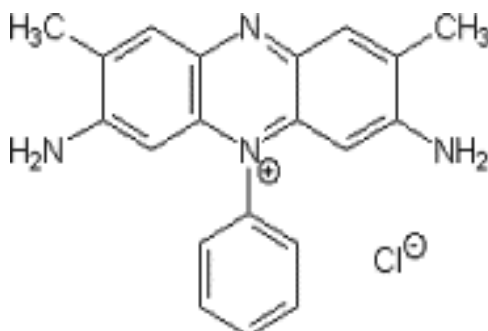
### I. Introduction

Dyes are used in almost every industry from textile to food industries to colour their products. Dyes or colouring substances are considered as one of the significant pollutants and they are stated as 'visible pollutant'. Most of dyes are toxic, mutagenic and carcinogenic which poses hazard to aquatic life as well as other living organisms [1]. Disposal of dyeing industry wastewater pose one of the major problems, because such effluents contain number of contaminants, and odour, and colour. Out of these, colour is the first contaminant to be recognized because it is visible to the human eye. Removal of many dyes by conventional waste treatment methods is difficult since these are stable to light and oxidizing agents and are resistant to aerobic digestion. Possible methods of colour removal from textile effluents include chemical oxidation, froth flotation, adsorption, coagulation etc. Among these, adsorption currently appears to offer the best potential for overall treatment, and it can be expected to be useful for a wide range of compounds, more so than any of the other listed processes. Recognizing the high cost of activated carbon, many investigators have studied the feasibility of cheap, commercially available materials as its possible replacements. Such materials range from industrial waste products such as waste tyres, bagasse blast furnace slag, fly ash, zeolites and lignin to agricultural products such as wool, rice husk, coconut husk, saw dust, peat moss etc. [2-11]. A number of low-cost adsorbents such as activated carbon prepared from various wastes [12-15], diatomaceous earth [16], industrial waste products [17], bagasse fly ash [18], clay mineral [19], biodegradable waste [20], hydrotalcite [21], coffee grounds [22], dusts [23], kudzu [24], 'waste' metal hydroxide sludge [25], agricultural waste [26], dolomitic sorbents [27], charcoal from extracted residue of coffee beans [28], bentonite and polyaluminum hydroxide [29] have been studied for adsorption of different dyes from solutions.

Fly ash is a waste substance from thermal power plants, steel mills, etc. that is found in abundance in the world. Since wide scale coal firing for power generation began in the 1920s, many millions of tonnes of ash and related by-products have been created. In India about 160 MT of fly ash is generated from burning of coal in power plants. As a matter of fact, the disposal of fly ash will soon be too costly if not forbidden. Throughout the world, much research is being conducted on the use of waste materials in order to either avert an increasing toxic threat to the environment or to streamline present waste disposal techniques by making them more affordable. It, therefore, follows logically that an economically viable solution to this problem should include utilization of waste materials in new products for other applications rather than disposal in a landfill. In recent years, utilization of fly ash has gained much attention in public and industry, which will help reduce the environmental burden and enhance economic benefit.

Safranin dye is one of the most commonly used azine dye, which are amongst the oldest known synthetic dyes. The structure of Safranin is shown below. It is a water-soluble reddish brown powder, which is mainly used as food dye in flavoring and coloring candies and cookies. It is also used for dyeing tannin, cotton, bast fibers, wool, silk, leather and paper. Due to its extensive use in food and textile industries as colorant,

Safranin has been considered as the model compound to represent the dyes that are released in effluents from the textile and food industries. Exposure to these effluents may be irritating to respiratory systems, skin, and digestive tract infections when ingested [30]. It is therefore, necessary to decolorize waste water to the lowest permissible concentration in order to safeguard the water bodies as stated by environmental regulations.



Scheme 1: Safranin dye

The objective of the present investigations has been to evaluate the efficiency of removal of Safranin dye using coal based fly ash which is easily available, cheap, and economically advantageous. In the present study application of fly ash for removal of Safranin dyes from aqueous solution has been studied. The effects of adsorbent dose, pH, temperature, initial dye concentration, and equilibrium time have been studied and obtained results are discussed.

## II. Materials and Methods

### 2.1 Safranin dye

Safranin is a cationic red dye having chemical formula C<sub>20</sub>H<sub>19</sub>CIN<sub>4</sub>; MW, 350.84g mol<sup>-1</sup>; IUPAC name as 3, 7-Diamino-2, 8-dimethyl-5-phenylphenazinium chloride) was supplied by Merk, India and used as adsorbate. A stock solution 1000ml was prepared by dissolving a weighed amount (1.0g) of safranin in one liter distilled water. Different concentrations were prepared by diluting the stock solution with suitable volume of distilled water and the natural pH of the stock solution was around 5.6. All the reagents used were of analytical grade.

### 2.2 Fly ash collection and adsorbent development

A representative sample of the fly ash was collected from H.E.G. Thermal Power Station, Mandideep, Bhopal, India. The fly ash was in the form of small, spherical grayish black particles. The collected sample was sieved to a desired particle size ranges (150 μm). Sample was washed with distilled water five times to remove the adhering organic materials and then dried in an oven at 110 °C for 24 h, and finally stored in vacuum desiccators.

### 2.3 Equipments and characterization of fly ash

The pH measurements were made using a pH meter (model CT Cl-46, Toshniwal Instruments, Delhi, India). The chemical constituents of fly ash were analyzed using Bruker S-8 Tiger WDXRF. The surface area was measured with a model QS-7 Quantasorb surface area analyzer. The specific gravity was determined using specific gravity bottles. The Scanning Electron Microscopy (SEM) was carried out using model LEO 438 VP, UK to study micro structure and qualitative characteristics of the ash of the fly ash. The identification of the mineralogical constituents and phase properties of fly ash was examined by Bruker D-8 advance X-ray diffractometer with a Cu-anode. The diffractometer was operated at 40 kV and 40 mA for 1 h over the range of 2θ from 0° to 80°. The infrared spectrum of the adsorbent was recorded in potassium bromide and Nujol mull in the range of 500-4000<sup>-1</sup>Cm using a Perkin Elmer spectrophotometer. All color measurements were made on a Spectronic 20D+ Thermospectronic spectrophotometer in the visible range in absorbance mode. Absorbance values were recorded at the wavelength of maximum absorbance of dye (Safranin) and dye solution was initially calibrated for concentration in terms of absorbance units. The concentration of dye was measured with a 1cm-path-length cell at a wave length (λ<sub>max</sub>) of 518 nm.

### 2.4 Sorption procedure

Adsorption of Safranin was carried out by a batch technique in aqueous suspensions using fly ash as adsorbent and experiments were conducted to observe the effect of various parameters such as pH, temperature, amount of adsorbent, initial adsorbate concentration, and contact time. Adsorption isotherms were recorded at

equilibrium conditions for concentration of dyes over the range 5-50 mg/l at a fixed pH (9.0) and temperature (303 K). The selected concentration range was ascertained after a good deal of preliminary examination. Adsorption study was made in a mechanically agitated 100-ml Erlenmeyer flask filled with 20 ml of dye solution of desired concentration along with a known amount of adsorbent. When the equilibrium was thought to be established, supernatant was carefully filtered through Whatmann filter paper (No. 41) and analyzed spectrophotometrically by measuring the absorbance at  $\lambda_{max}$  of 518 nm. A stock solution (1g/l) of the dye was prepared in distilled water. It was diluted to the required volume and concentration. The experiments were performed in duplicate and the average results were reported. The amount of dye adsorbed at time  $t$ ,  $q_t$  (mg/g), was obtained by calculating the difference between the initial and the final safranin concentration as shown in equation 1:

$$q_e = (C_0 - C_e) \times V/W \quad (1)$$

Where  $q_e$  (mg/g) is the amount of dyes adsorbed, and  $C_0$  (mg/l) is the initial dye concentration, while  $C_e$  (mg/l) is the concentration of dye in solution at equilibrium,  $V$  (L) is the volume, and  $W$  (g) is the weight of adsorbent. The percentage removal of the dye was computed using the following equation

$$\text{Percentage of removal (\%)} = (C_i - C_e) \times 100/C_i \quad (2)$$

Where  $C_i$  and  $C_e$  are the initial and equilibrium concentration of dye (mg/l) in solution.

### 2.5 Adsorption isotherms

The adsorption equilibrium models often provide insight into the sorption mechanism, surface properties and affinity of adsorbent. The most commonly used equilibrium models are Langmuir and Freundlich isotherms [32].

Langmuir isotherm is based on the assumption that maximum adsorption corresponds a saturated monolayer of solute on homogenous adsorbent surface. It comprised of a finite number of identical sites with homogeneous adsorption energy. A basic assumption states takes sorption takes place at specific homogeneous sites within the adsorbent. Once a dye molecule occupies a site, no further transmigration can take place at the same site. The total monolayer capacity of the adsorbent is equal to  $Q_0$ , a Langmuir constant. The rearranged Langmuir isotherm is represented by following equation:

$$C_e/q_e = 1/Q_0 b + C_e/Q_0 \quad (3)$$

where,  $C_e$  is the equilibrium concentration of dye (mg/l),  $q_e$  is the amount of dye adsorbed at equilibrium (mg/g),  $Q_0$  is the monolayer adsorption capacity (mg/g), and  $b$  is the constant related to the free energy of adsorption. Hence, a plot of  $C_e/q_e$  versus  $C_e$  yields a straight line with  $Q_0$  calculated from the slope and the value of  $b$  as its intercept.

Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface or surface supporting sites of varied affinities it. Due to variation of interactions between the adsorbed molecules sites with of stronger affinity are occupied first, and in this way multilayer setting of adsorbate molecules takes place. The validity of the Freundlich isotherm model was proved by using following relation: Freundlich isotherm is an exponential equation and can be written as:

$$q_e = K_F C_e^{1/n} \quad (4)$$

$$\log q_e = \log K_F + 1/n \log (C_e) \quad (5)$$

where,  $K_F$  is the constant indicative of the relative adsorption capacity of the adsorbent (m/g), and  $1/n$  is the constant indicative of the intensity of the adsorption. The Freundlich equation possesses two constant,  $K_F$  and  $1/n$ . High and low values of  $K_F$  and  $1/n$  indicate high adsorption throughout the concentration range studied whereas high values of  $1/n$  and low values of  $K_F$  show low adsorption. When  $1/n = 1$ , the adsorption is favorable.

### 2.6 Kinetic studies

Intraparticle diffusion is the most common technique used for identifying the mechanism involved in adsorption process. In order to investigate the mechanism of the Safranin adsorption onto fly ash adsorbent, intraparticle diffusion based mechanism was studied. Kinetic studies were carried out in batch at 10 mg/l of initial dye concentration with a fixed dose of adsorbent dose of 20 g/l at 303 K and pH 9.0. After a fixed time interval the adsorbent was separated by filtration and the filtrate thus obtained was analyzed

spectrophotometrically to determine the equilibrium concentration of the dye. The study of kinetics of adsorption describes the solute uptake rate at the solid-solution interface. The rate constant of adsorption of dyes on to fly ash,  $K_{ad}$  has been studied using the Lagergren first order rate equation:

$$\log (q_e - q_t) = \log q_e - K_{ad} t / 2.303 \tag{6}$$

where,  $q_e$  is the amount of dye adsorbed at equilibrium, and  $q_t$  is the amount of dye adsorbed at time  $t$  (both in mg/g).

### III. Results and Discussion

#### 3.1 Characterization of fly ash

The chemical composition of fly ash determined by WDXRF has been shown in Table 1 which shows that the major constituent of the fly ash is  $SiO_2$ , (55.26 %) followed by  $Al_2O_3$  (22.75 %),  $Fe_2O_3$  (7.12 %), CaO (4.10 %) and MgO (0.63 %). The fly ash predominantly consists of trace metals with the chief constituents being oxides, silicates and aluminosilicates of calcium, iron and other bases. These oxides have a tendency to form metal hydroxide complexes in the solution and the subsequent acidic or basic dissociation of these complexes at the solid-solution interface leads to the development of a positive or negative charge on the surface. The surface area of fly ash is  $2.89 \text{ m}^2/\text{g}$  and specific gravity is  $2.2 \text{ g/cm}^3$ .

The results of SEM investigation are shown in Fig. 1 which reveals typical fly ash morphology and surface texture. Most of the particles present in the fly ash are sub-angular and spherical in shape. The image also reveals that the particles present in the fly ash are covered with relatively smooth grains of quartz, clusters of iron (Fe-oxide). Irregular surface of glass matrix is observed which may be responsible for an increase in adsorbent pore volume.

The diffractogram (Figure 2) shows the X-ray diffraction pattern of fly ash for particle size  $\leq 45 \mu\text{m}$ . It is observed that the fly ash consists mostly of mullite, quartz, hematite and a small amount of hematite and calcium oxide with large characteristic peaks of quartz ( $SiO_2$ ). This result is similar to that reported for a fly ash investigated by Sarkar et al. [33]. The intensity of quartz is very strong with mullite forming a chemically stable and dense glassy surface layer. The low calcium oxide intensity is characteristic of low-Ca Class-F fly ash.

The infrared spectrum of fly ash (Fig. 3) shows broad and weak peaks in the region of  $4000\text{-}500 \text{ cm}^{-1}$  associated with the functional groups that are on the surface of coal fly ash. The band appearing at  $560 \text{ cm}^{-1}$  is associated with octahedral aluminium present in mullite. In addition, bands appearing between  $800\text{-}600 \text{ cm}^{-1}$  are associated with tetrahedral vibrations formed which are known as secondary building units and fragments of aluminosilicate system. Band appearing at  $2360 \text{ cm}^{-1}$  could be attributed due to alkyl groups that are present in clay material of coal fly ash. Bands appearing at  $800\text{-}1200 \text{ cm}^{-1}$  and  $450\text{-}550 \text{ cm}^{-1}$  assign to asymmetric stretching mode and bending mode of T-O bond respectively. These bands are more or less dependent on the crystal structure. The mid infrared region of the spectrum contains the fundamental framework vibrations of  $Si(Al)O_4$  groupings. Although some interference can be made about surface functional groups from IR spectra, the weak and broad bands do not provide any definitive information about the nature of the surface oxides. The data, however, indicate the presence of some surface groups on the adsorbent material.

**Table 1:** Chemical constituents of the fly ash

Constituents	Weight %
$SiO_2$	55.26
$Al_2O_3$	22.75
$Fe_2O_3$	7.12
CaO	4.10
$TiO_2$	2.95
$K_2O$	2.14
$P_2O_5$	1.65
$SO_3$	1.58
$Na_2O$	1.23
MgO	0.63
LOI	4.10

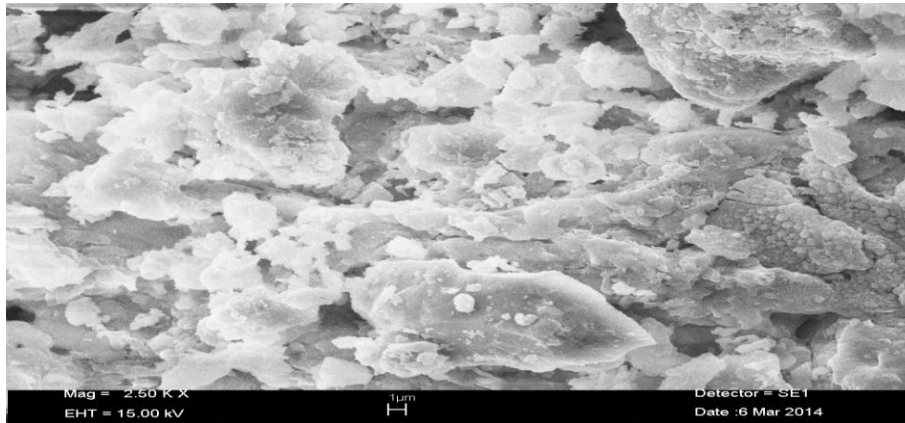
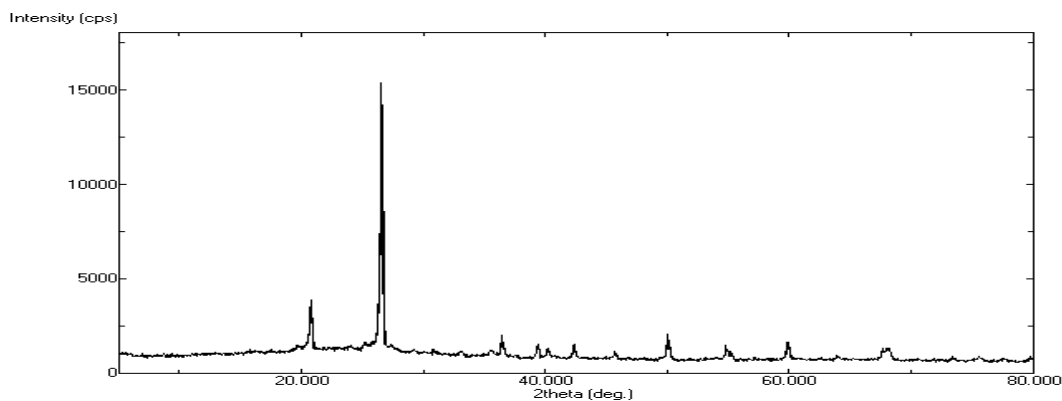


Fig.1: Scanning electron micrograph (SEM) of fly ash



X-ray diffraction pattern of fly ash

Fig. 2:

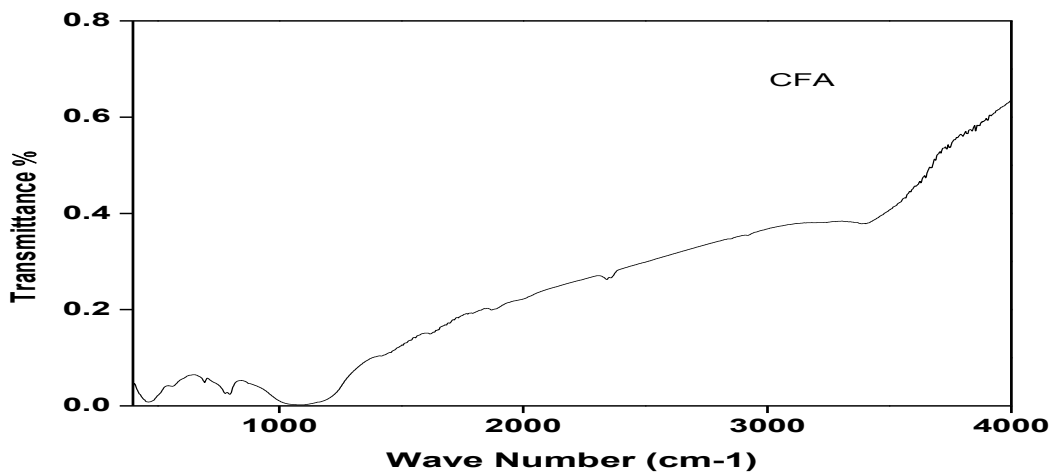


Fig.3: FTIR of coal fly ash

### 3.2 Sorption Studies

#### 3.2.1 Effect of contact time

To study the effect of contact time of Safranin dye on adsorption behavior two concentrations (5 and 10 mg/l) were used with a fixed adsorbent dose of 20 g/l at 303 K and at a natural pH 6.8. The contact time was varied from 15 min to 300 min for both the concentrations studied. The percentage efficiency of dye adsorption were calculated and plotted in Fig. 4. A perusal of Fig. 4 indicates that the efficiency of dye absorbed was rapid in initial stage up to 120 min and after that decreases due to saturation of the active site which do not allow further adsorption to take place It is also observed that at higher concentration of Safranin (10 mg/l), the absorption efficiency is high (74.6 %) as compare to the maximum efficiency of 72.8 % for 5 mg/l after 120 min of contact time. The observed increase in the adsorption of dyestuffs with increasing concentration may be due to sufficient adsorption sites at adsorbent [34]. The optimal contact time to attain equilibrium was experimentally found to be about 120 min.

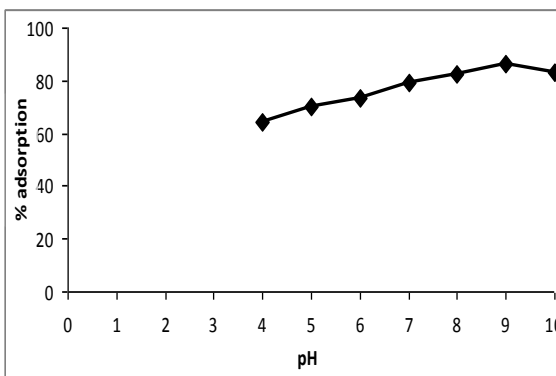
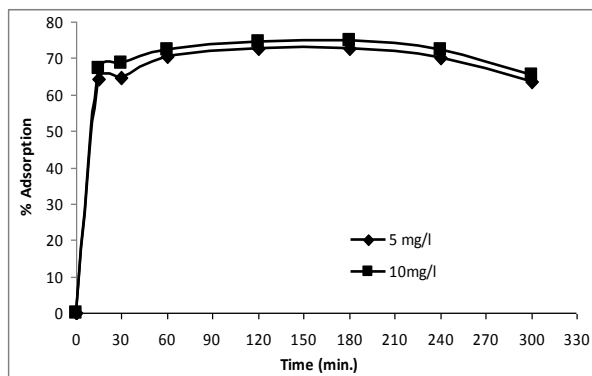


Fig. 4: Effect of contact time on Safranin dye adsorption Fig. 5: Influence of pH on Safranin dye adsorption

### 3.2.2 Effect of pH

To determine the optimum pH conditions for the adsorption of Safranin on fly ash, the effect of pH was observed over the pH range (4.0–10.0). The studies were conducted at a fixed concentration of adsorbate (10 mg/l), contact time (120 min) and adsorbent dose 20 g/l at 303 K. pH was adjusted by adding either 0.1M HCl or 0.1M NaOH. The results obtained are presented in Fig. 5, which show that adsorption of Safranin increases with increase in pH from 4.0 to 9.0 and after that a decrease in absorption capacity has been observed on further increase in pH to 10.0. Maximum adsorption of Safranin is 86.5 % at an optimum pH of 9.0. The probable reason for this is that silica and alumina, which are chief constituents of fly ash, form metal-hydroxide complexes in solution and the subsequent acidic or basic dissociation of these complexes at the solid-solution interface leads to either positive or negative surface charge. At acidic pH, the dissociation of the metal-hydroxide complexes causes the surface to become positively charged. However, with increasing pH, the surface becomes negatively charged as in the alkaline medium the silica and alumina get converted into  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  type of functional sites and, therefore, the binding of positively charged dyes onto these surfaces become much favorable resulting in enhanced adsorption of dyes. The variation of adsorption with pH can be explained by considering the difference in the structure of the dyes, as well as the point of zero charge of the fly ash (which is 5.8). The main constituents of fly ash are silica and alumina. The ZPC (a concept; related to the adsorption process; describes the condition when the electrical charge density on a surface is zero) of silica is 2.3, while that of alumina is 8.2, and as such the surface of fly ash would have high positive charge density below pH value of 5.8, i.e. ZPC of the fly ash. Under these conditions the uptake of positively charged dyes would be low; with increasing pH, the negative-charge density on the surface increases resulting in enhanced removal.

### 3.2.3 Influence of adsorbent dosage

To investigate the effect of mass of adsorbent on the adsorption of Safranin, a series of adsorption experiments was carried out with different adsorbent dosage varied from 5 to 25 g/l at an initial dye concentration of 5 and 10 mg/l at natural pH of 9.0 and temperature 303 K. The contact time was kept 120 min and the results are shown in Fig. 6. It is observed that the percentage removal efficiency of Safranin increases initially with increase in adsorbent dose from 5 to 20 g/l and after that a decrease has been observed. The maximum efficiency at a dose of 20 g/l is 90.5 and 92.2 % for 5 and 10 mg/l of dye concentration respectively. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase in adsorbent dosage. The decrease in efficiency at higher adsorbent dose may be attributed to the overcrowding of adsorbate molecules which prevent the diffusion through the actual adsorption sites.

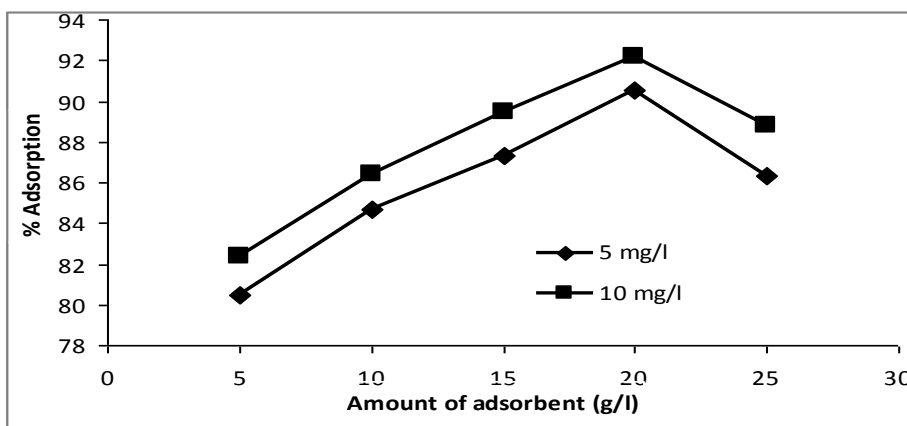


Fig. 6: Effect of adsorbent dose on Safranin dye adsorption on fly ash

### 3.2.4 Effect of adsorbate concentration and temperature

The effect of initial concentration of Safranin between the ranges of 5 to 50 mg/l was carried out to observe the absorption efficiency at a fixed adsorbent dosage (20 g/l) and temperature (303 and 313 K). The pH was maintained at 9.0. and contact time was kept 120 min. The results of the studies are shown in Fig. 7 which depict that dye uptake increases with increase in initial Safranin concentration from 5 to 40 mg/l and thereafter equilibrium is achieved in dye uptake efficiency at a concentration of 50 mg/l at 303 and 313 K. However, the uptake of dye was higher at 303 K with a dye uptake efficiency of 2.43mg/g of adsorbent. The increment in sorption capacity may be due to the increase of dye concentration which resulted in higher concentration gradient of the dye, thus leading to higher sorption capacity. The rate of uptake of dye was found to decrease with increase in temperature, thereby indicating the process to be exothermic in nature. This decrease in adsorption efficiency on increase in temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate.

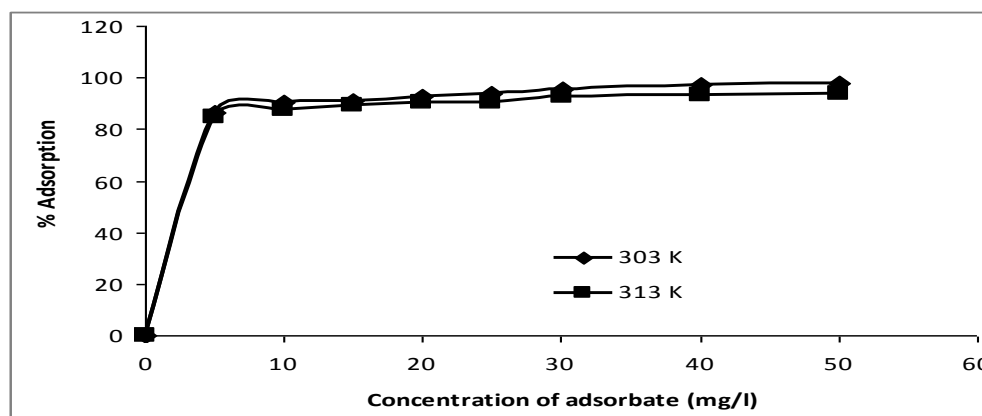


Fig. 7: Effect of adsorbate concentration and temperature on Safranin dye adsorption on fly ash

### 3.3 Adsorption isotherms

The adsorption of Safranin at equilibrium with increase in initial dye concentration at 303 K has been fitted in Langmuir model and Freundlich isotherms. In Langmuir isotherm,  $1/q_e$  (mg/g) has been plotted against  $1/C_e$  (mg/l) a straight line with slope  $1/bQ_0$  is obtained as shown in Fig. 8. A perusal of Fig. 8, shows that the adsorption of Safranin follows the Langmuir isotherm. Langmuir constants  $Q_0$  and  $b$  are calculated and the values of these constants are given in Table 2 along with coefficient of correlation ( $R^2$ ). The maximum adsorption capacity ( $Q_0$ ) was 1.7633 mg/g.

Table 2: Freundlich and Langmuir isotherm parameters at 30°C

Freundlich parameters			Langmuir parameters		
$K_F$	$1/n$	$R^2$	$Q_0$ (mg/g)	$b$	$R^2$
1.0814	0.2481	0.9014	1.7633	2.1239	0.964

The equilibrium adsorption data has also been data fitted in the linear form of Freundlich isotherm model and the plots of  $\log q_e$  against  $\log C_e$  shown in Fig. 9 are linear and the values of  $K_F$  and  $1/n$ , calculated from intercept and slope of the plot (Figure 9), respectively, are given in Table 2. The calculated values of  $1/n$

are less than 1, which suggest the favorable adsorption of dye onto the fly ash. The values of the regression coefficients indicate that the data satisfactorily follow both Langmuir and Freundlich models but the Langmuir isotherm fits the experimental data better.

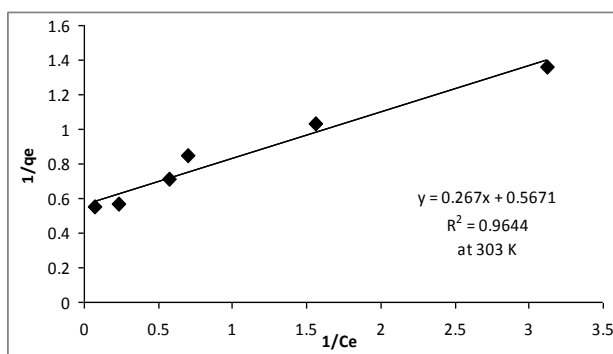


Fig.8: Langmuir isotherm plot of Safranin dye

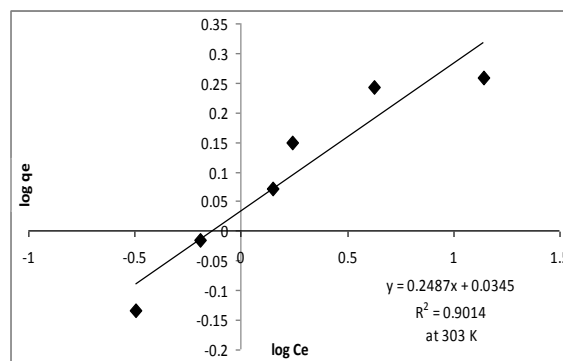


Fig.9: Freundlich isotherm plot of Safranin dye

### 3.4 Kinetic studies

The graph (Fig. 10) obtained for  $\log(q_e - q_t)$  versus time (t) in minutes exhibits straight lines and confirm the adsorption process to follow first order rate kinetics in each case. The  $K_{ad}$  value calculated from slope of the plot ( $K_{ad}/2.303$ ) is  $0.0115 \text{ min}^{-1}$ .

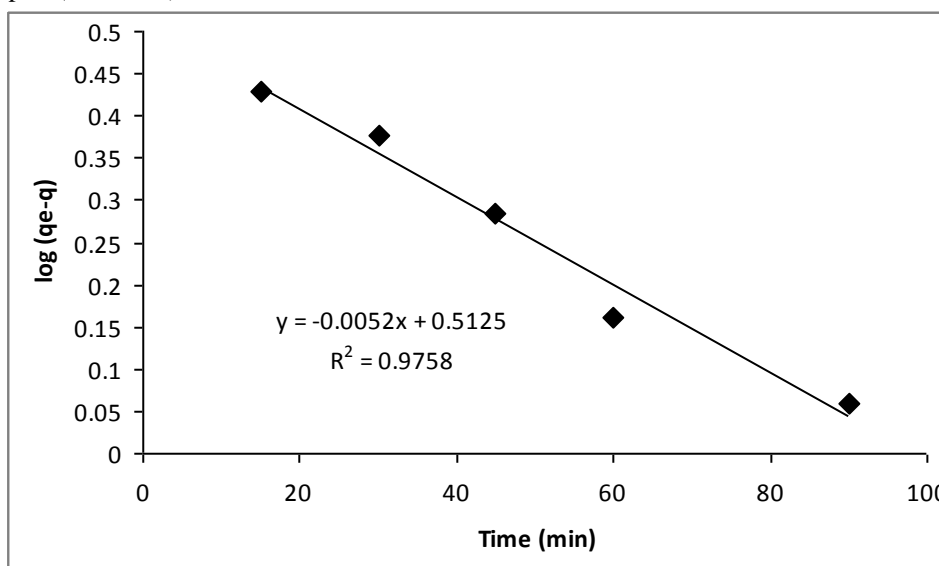


Fig.9: Langergren's plot of Safranin dye adsorption on fly ash

## IV. Conclusions

The studies presented revealed that fly ash from thermal power plants can be fruitfully employed as adsorbent for the removal of Safranin dye. The pH was found to be significant factor which affects the adsorption capacity of safranin. The removal of Safranin, a cationic dye is about 97 % at 40 mg/l with a dose of adsorbent of 20 g/l and pH 9.0 at 303 K. The optimum contact time was found to be 120 min. The adsorption process was of first order; physical and exothermic in nature. The adsorption data was analyzed by Langmuir and Freundlich models and fitted well. The fitness of Langmuir's model indicated the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent. The developed adsorbent is quite cheaper than commercially available activated carbons, while their performance is comparable. Utilization of fly ash will solve not only its disposal problems and environmental hazards, but also help as potential adsorbent for removal of dyes from waste waters.

## Acknowledgements

Authors (MKD, PS and CA) are grateful to MPCOST, Bhopal (MP) for providing financial assistance to carry out the present work.



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