Evaluation of Flyash for Removal of Rhodamine-B from Aqueous Solution

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Abstract: **The physio-chemical property of flyash from Suratgrah thermal power plant was investigated for the adsorption of the Rhodamine-B. The adsorption was done for different purposes. The effects of contact time, flyash amount, dye concentration, pH and temperature in the Rhodamine-B removal were examined. The results indicated that the main mechanism for Rhodamine-B removal was precipitation due to the alkaline characteristics of fly ash. The results show that the sorption isothermal data could be well described by Freundlich and Langmuir model.**

Keywords: **Flyash, Rhdamine-B, Freundlich and Langmuir model**.

I. INTRODUCTION

Coal firing power thermal stations are still the main source of power generation in India. Flyash from Suratgrah Thermal Power plant was investigated for its physio-chemical properties. It has been confirmed that the utilization of fly ash would solve both disposal problem and served as a cheaper material for adsorption of water pollutants. The chemical characteristic of fly ash which depends strongly on the geological origin of the coal, method and condition of combustion would be one of the important factors to be considered. Adsorption, which is a surface phenomenon, that depends on the higher specific surface area, narrow particle size distribution and the porosity of an adsorbent were investigated and observed that the larger the specific surface area, the higher the carbon content and the finer the particle size of the fly ash the greater its adsorption capacity[1].

In the present study, the physio-chemical properties of flyash from Suratgrah thermal power plant were determined. The adsorption experiment was done to quantify the effects of different parameters in the light of the chemical and physical properties of the fly ash. The effects of contact time, flyash amount, dye concentration, pH and temperature on Rhodamine-B removal were examined.

II. MATERIALS AND METHODS

Physio-Chemical Analysis: The chemical composition of the flyash sample was determined by tritrimetric method for the quantitative evaluation of the sample. The particle size of the fly ashes was measured using a laser based particle size analyzer, CILAS Particle Size Analyzer 1064. The Scanning Electron Microscopy (SEM) model Carl Zeiss AVO 18 was used to determine the morphological and qualitative characteristics of the ash.

Batch Adsorption Study: Batch mode adsorption studies for Rhodamine-B was carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dose, agitation time, temperature and pH [2]. Solution containing adsorbate and adsorbent was taken in 250 mL capacity beakers and agitated at 150 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using Whatman No.1 filter paper. To avoid the adsorption of adsorbate on the container walls, the containers were pretreated with the respective adsorbate for 24 hours. A graph is to be plotted with % Removal vs parameter after calculating the value of Qe.

$$\% \text{ Removal} = \frac{\text{Co}-\text{Ce}}{\text{Co}} * 100 \qquad \text{Eq. 1}$$

Where,

Co = intial concentration of the dye(mg/l)
Ce = equilibrium concentration of the dye(mg/l)
V = volume of the dye solution(l)
m = weight of the adsorbent(g)

Freundlich and Langmuir isotherm: The Langmuir isotherm represents the equilibrium distribution of dye molecules between the solid and liquid phases [3]. The following equation can be used to model the adsorption isotherm:

$$Ce/ Q e = 1/ (Q_0 b_L) + 1/Q_0 \, Ce \qquad \text{Eq. (2)}$$

Where,
C_e = equilibrium concentration of adsorbate in the solution (mg/l),
Q_e = amount of adsorbate adsorbed per mass of adsorbent at equilibrium (mg/g),
Q_0 = maximum adsorption capacity
b_L= adsorption equilibrium constant related to the sorption energy between the adsorbate and adsorbent (l/mg) .

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined by

$$R_L = 1/1+bCo \qquad \text{(Eq. 3)}$$

Where,

Co = initial adsorbate concentration (mg/L)
b = Langmuir constant(L/mg).

The parameter indicates the shape of the isotherm as follows, depending on R_L values

If R_L>1 then favourable, R_L=1 then linear, 0< R_L<1 favorable and R_L=0.

The Freundlich isotherm is represented by the equation (Freundlich, 1906) [4]:

$$\text{Log } Q_e = \log K + 1/n \log C_e \qquad \text{(Eq. 4)}$$

Where,

Ce = equilibrium concentration (mg/l),
Qe = amount adsorbed (mg/g),
K = adsorption capacity,
n= adsorption intensity.

The n values for the dyes were between 1 and 10 under the studied conditions, indicating beneficial adsorption.

III. RESULT AND DISCUSSION

The chemical analysis of the fly ash was carried out by routine chemicals analysis is presented in Table 1. The sum of the SiO_2, Al_2O_3 and Fe_2O_3 fractions was 93.96%. The loss on ignition (LOI), an indication of unburned carbon, was 1.13%, a relatively low value. The sum of the elemental oxides does not equal 100% due to the presence of unreported trace elements. According to ASTM C618 standards [5], the fly ash is divided into two types. If the sum of SiO_2, Al_2O_3, and Fe_2O_3 is more than 70%, it is named type F. If the sum is upto 50%, it is named type C. The fly ash is class F fly ash with 93.96% of SiO_2, Al_2O_3 and Fe_2O_3 as a major constituent. The oxides of SiO_2, Fe_2O_3 and Al_2O_3 present in fly ash could adsorb either positive or negative contaminants. The central ion of silicates has an electron affinity, giving the oxygen atoms bound to it low basicity. This allows the silica surface to act as a weak acid, which can react with water, forming surface silanol (SiOH) groups and are amphoteric in nature [6].

The particle size of fly ash collected from Suratgrah Thermal Power plant was found to be

PARTICLE SIZE

- Minimum-0.04 µm
- Mean-13.90 µm
- Maximum-56 µm

The size range of the particles is wide i.e. 0.04 micron to 56 micron. Adsorption, which is a surface phenomenon that depends on the particle size distribution and it is observed that finer the particle size of the flyash the greater its adsorption capacity will be. Maximum cumulative density is found to be between 8 µm to 36 µm. Similarly Kara et.al also found the particle size distribution between 3.6 to181 µm [7]. Keeping this in mind, the flyash material was sieved with the sieve of 45 µm, so that maximum number of finer particle size flyash is obtained for the process of adsorption.

The SEM image clearly shows that the fly ash particles are mainly composed of irregular and porous particles due to the presence of a relatively high amount of unburned carbon. The microstructure of flyash consists mainly of compact or hollowed spheres of different sizes in such a way that some of the smaller size particles got adhered on bigger size particles. It is clear from Figure2 that flyash has considerable numbers of heterogeneous layer of pores where there is a good possibility for dye to be adsorbed.

Table 1 Bulk Chemical Analysis of a Fly Ash

Oxide	Mass %
Silicon Dioxide (SiO_2)	65
Aluminum Oxide (Al_2O_3) and Iron Oxide (Fe_2O_3)	28.96
Magnesium Oxide (MgO)	0.30
Sulfur Trioxide (SO_3)	0.07
Available Alkali as Na_2O_x	0.005
Loss on Ignition (LOI)	1.13

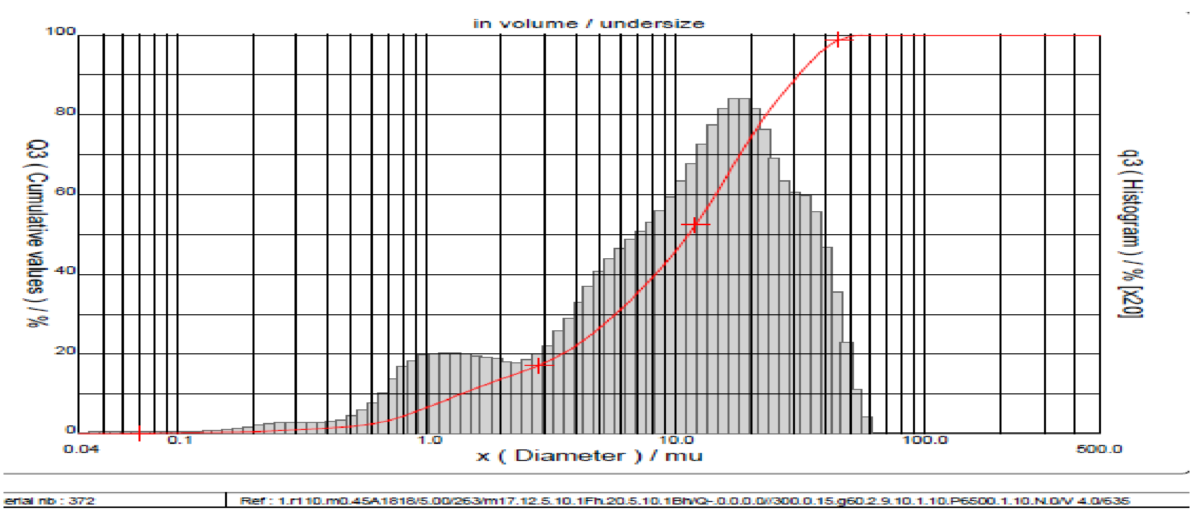

Figure 1 Particle Size Distribution of flyash

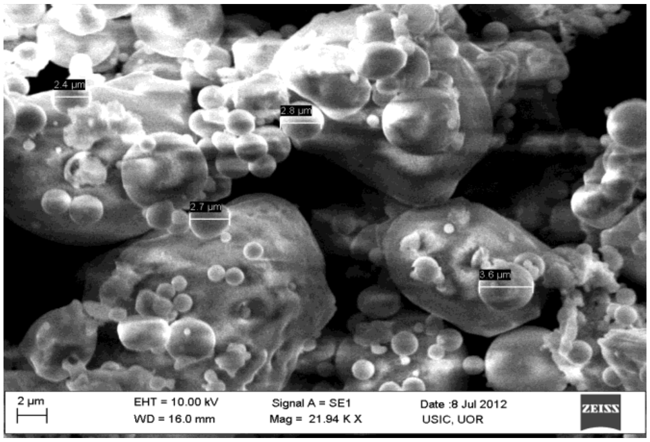

Figure 2. Typical SEM micrograph of fly ash (magnification: 2000×)

Batch adsorption Study on Rhodamine-B:

Contact Time: Figure 3 presents the result for the effect of contact time on the removal of Rhodamine -B at an initial concentration of 5 mg/L. The graphs are single and smooth, indicating monolayer coverage of the adsorbent surface by the dye. It is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is allowed. The final dye concentration did not vary significantly after 180 min.

Flyash Amount: From Figure 4 we see that the optimum dose for the Rhodamine –B is 1g/50ml. As seen in the Figure with the increase in adsorbent amount the % Removal decreases. This implies that the number of adsorption sites in the samples with m= 1g is sufficient for the complete adsorption of dye. In experiments with m > 1g no expected increase in adsorption of dye was observed. Evidently, in these experiments the content of dye in the solid and liquid phases achieved equilibrium concentrations [8].

Dye Concentration: Percentage removal of Rhodamine -B decreased from 91.16 to 76.89 % with increase in dye concentration as shown in Figure 5. The removal percentage decreases and the extent of adsorption increase with increasing initial dye concentration. This is obvious from the fact that the initial dye concentration provides an important driving force to overcome all of mass transfer resistance. It is because of that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration [9].

pH: There is no significant increase in amount adsorbed after pH 6 as shown in Figure 6. In the present study the pH was maintained at 7. Infact adsorption found to decrease with increase in pH of solution. The adsorption of these positively charged dye groups on the adsorbent surface is influenced by the charge on the flyash which in turn is influenced by the solution pH. The result showed that availability of negatively charged groups at flyash surface is necessary for the adsorption of dye to proceed which we see at pH -4 is almost unlikely as there is a net positive charge in the adsorption system due to the presence of H_30^+ .

Temperature: Temperature has important effects on the adsorption process. With the increase in temperature, rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of the adsorbent particle increases [10]. The result of studies for the adsorption of dye reveals that the percentage removal of Rhodamine - B at different temperature increased from 77.30% - 91.91% as shown in the Figure 7.

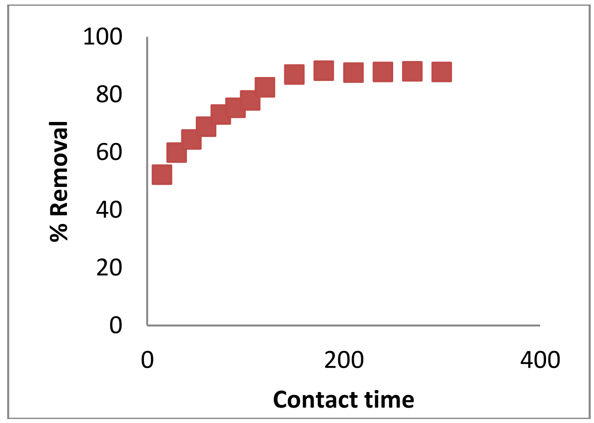

Figure 3 Effect of Contact Time on adsorption of Rhodamine-B

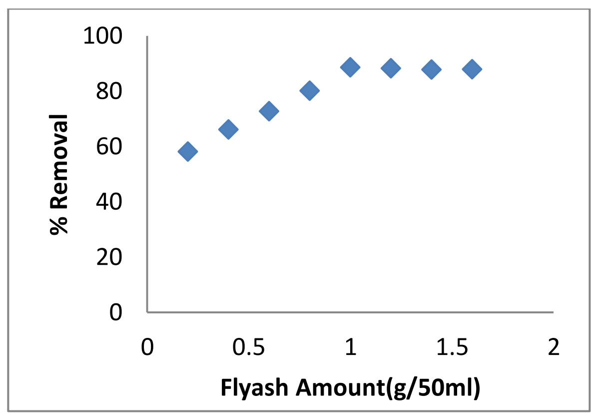

Figure 4 Effect of Flyash Amount on adsorption of Rhodamine-B

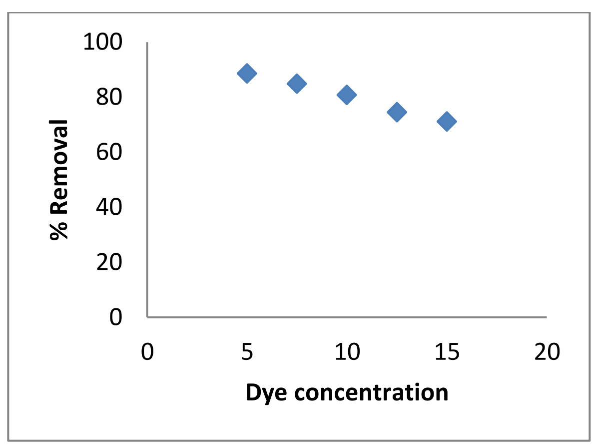

Figure 5 Effect of dye Concentration on adsorption of Rhodamine-B

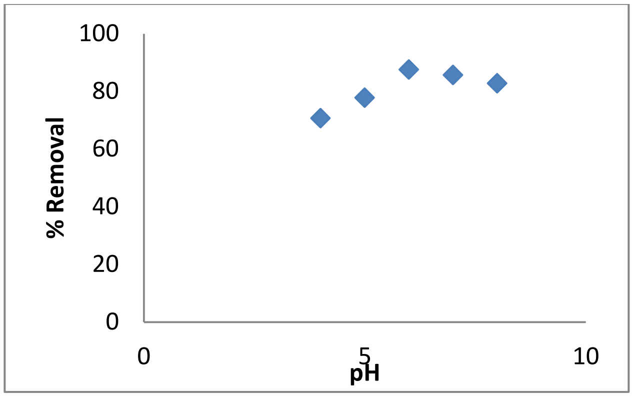

Figure 6 Effect of pH on adsorption of Rhodamine-B

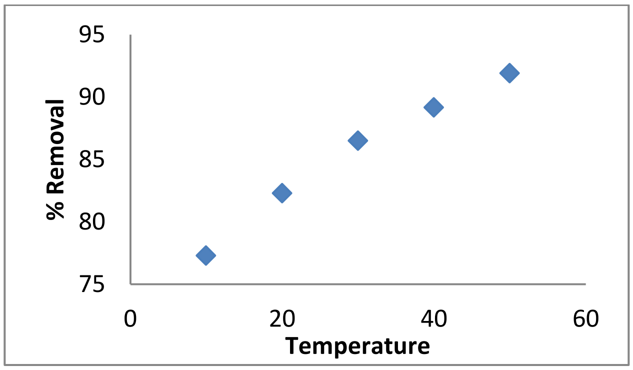

Figure7 Effect of Temperature on adsorption of Rhodamine-B

Freundlich and Langmuir Isotherm

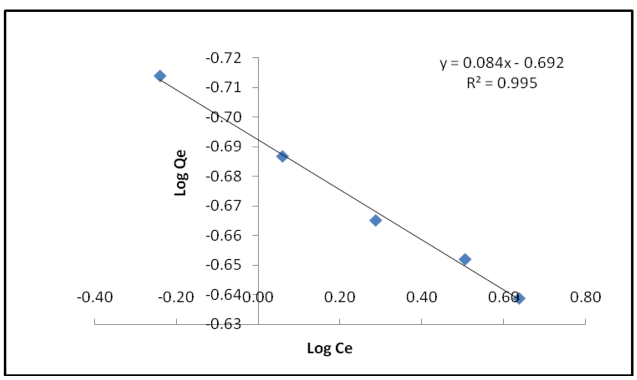

Figure 8 Freundlich Isotherm

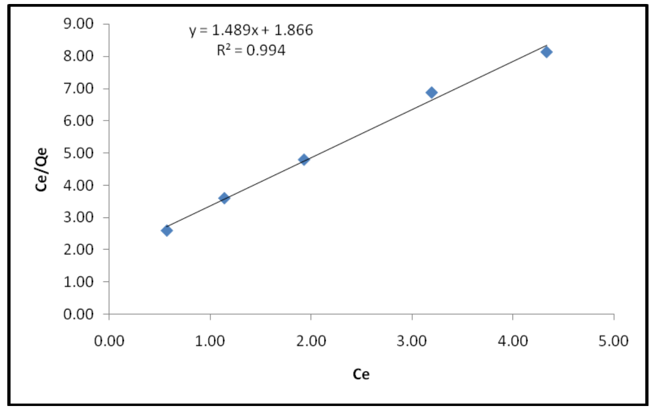

Figure 9 Langmuir Isotherm

Figure 8 and Figure 9 represent the Freundlich and Langmuir Isotherm for Rhoamine-B which are straight line indicating the favourable adsorption of the dye. R value is 0.200 (1>R>0) fits the favourable condition whereas n is 11.862.

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