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Research Article

Adsorption of Reactive Red 194 Dye from Textile Effluent by Using Class F Fly Ash

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Abstract: A low cost adsorbent Fly Ash was used for the removal of Reactive Red 194 dye (RR 194 dye) from textile effluent. The Fly ash was activated by chemical treatment by N/2 H_2SO_4. Batch adsorption experiments were performed as functions of adsorbent doses, initial dye concentration, contact time, and pH. The percentage of colour removal was increased with decreasing dye concentration and increasing contact time and adsorbent doses. Maximum removal of colour has been taken place in acidic medium (pH=5). Adsorption data was fitted on Langmuir and Freundlich Isotherm modal. From the experimental data it was found that the adsorption process using fly ash adsorbent could be well described by Langmuir modal than the Freundlich modal.

Keywords: Adsorption, Fly ash, Langmuir Isotherm, Reactive red 194 dye, Textile Effluent.

INTRODUCTION

Discharge of dye bearing waste water into natural streams from textile, paper, rubber, plastics, paints, printing, leather and carpet industries has created serious ecological problems due to persistent nature of dyes [1]. The problem is more severe for textile industries because they are major consumers of the dyes and they are responsible for discharging a large quantity of highly coloured waste water effluents into nearby land and rivers without any treatment which causes various adverse effects on aquatic ecosystem and human life [2] .Over 70,000 tons of approximately 10,000 types of dyes and pigments are produced annually throughout the world, of which about 20-30% are wasted in industrial effluent during textile dyeing and finishing processes [3]. The coloration of the water by the presence of dyes, even in small concentration is easily detectible. These dyes usually have a synthetic origin and complex aromatic molecular structure, which make them more stable and more difficult to biodegrade. They have an inhibitory effect on the process of photosynthesis and, thus, affecting the aquatic life. Many dyes may also cause allergic dermatitis, skin irritation, dysfunction of kidney, liver, brain, reproductive and central nervous system. Besides, some are suspected carcinogens and mutagens [4].

The wastewater produced by textiles and other industries is currently the most important environmental issues at Panipat, (Haryana) India. Coloured wastewater is particularly associated with reactive azo dyes that are generally used for dyeing carpet, cotton, wool, silk, and nylon and it is also used in the manufacturing of paints [5]. Now-a-days, these dyes make up approximately 30% of the total dye market. Reactive dyes are the most common dyes used at Panipat due to their advantages, such as bright colours, excellent colour fastness and ease of application but due to low biodegradability under aerobic conditions these dyes are toxic and carcinogenic in nature [6].

Thus, the removal of dyes from coloured effluents of textile industries is one of the major concerns these days. Various techniques like chemical coagulation [7], foam flotation [8], electrolysis, chemical oxidation [9], photochemical degradation [10], membrane filtration [11], biological treatment, adsorption [12] have been used in the past for the removal of dye from the textile effluents. Most of these techniques are rather expensive and not so effective. But adsorption process has found to be more effective and cheap for the removal of colour from the effluent samples. Although the activated carbon is most effective for the adsorption of dyes, but it is quite expensive due to non- renewable and relatively expensive starting material such as coal. Therefore, the development of low cost alternative adsorbents has been the focus of recent research [13]. Many researchers have utilized a number of substances such as agriculture waste: coir pith [14], banana pith [15], sugarcane dust [16], sawdust [17], rice husk [18], orange peel [19], apple pomace and wheat straw [20], neem husk [21], wood material, industrial solid wastes: fly ash, bottom ash, red mud [22-23], shale oil ash etc.

Fly ash is one of the waste materials originating in great amounts in combustion processes. In other words, Fly ash is a kind of waste product generated from Thermal Power Plants, which is the major cause environmental pollution. Although, significant quantities of fly ash are being used in various applications, but large quantity of this is not used and this requires disposal. For reducing environmental pollution, research is, therefore, needed to develop new environment friendly applications that can further exploit fly ash [24]. Many researchers have been used fly ash as adsorbent for the removal of colour [25-28].

In the present study, the Fly Ash was activated and characterized. The effects of mixing time, adsorbent doses, initial dye concentration and pH on adsorption of reactive red194 dye (RR 194 dye) from effluent sample by fly ash under equilibrium conditions were investigated. The data was treated with the help of two empirical models to predict the percentage of removal and quantity adsorbed of dye. Adsorption data was fitted on Langmuir and freundlich isotherm modal.

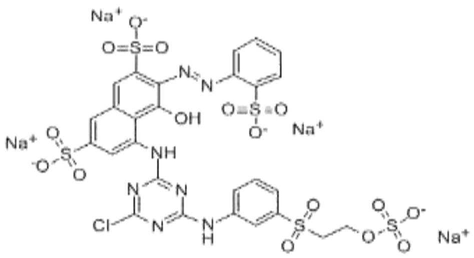

Figure1: Chemical structure of reactive red 194 dye

MATERIAL AND METHODS

Dye Characterization

The dye used in the present study is Reactive Red 194, obtained from Rivera Textiles at Panipat (Haryana) in India. It was received without any further purification. Its characteristics are summarized in table 1. Its chemical structure is shown in fig.1. The Absorbance values were recorded by Systronics UV-VIS Spectrophotometer-117 at the maximum wavelength 540 nm.

Table 1: Characterization of Reactive Red 194 dye

Chemical name	Reactive red 194
Molecular Formula	$C_{27}H_{18}ClN7Na_4O_{16}S_5$
Formula Weight	984.21
Chromophore	Azo
Maximum absorbance(λ_{max}) nm	540
Water solubility	100%
pH value(50mg/l)	8.6

Fly Ash

Fly Ash collected from the Thermal Power Plant, Panipat (Haryana) India was washed several times with distilled water and left to dry and, then, subjected to chemical activation. Fly Ash sample was soaked in N/2 H_2SO_4 solution for 24 hrs. Then it was filtered and dried into oven at 60^0C for over night. The physical characteristics and chemical composition of fly ash are reported in table 2 and 3, respectively. Fly Ash used in the present study is suitable for class F Fly Ash because CaO is below than 10 % and SiO_2 is higher than 50 %. It is produced by the burning of bituminous coal.

Table 2: Physical characteristics of Fly Ash

Specific Gravity	2.06
Bulk Density	1189 Kg/m3
True Density	1.40g/cc
Acid Insoluble	87.3% By wt.

Table 3: Chemical composition of fly ash

Component	Weight %
SiO_2	68.25% By wt.
Al_2O_3	19.02% By wt
Fe_2O_3	4.64% By wt.
CaO	3.42% By wt.
MgO	Absent
K_2O	Absent
Na_2O	Absent
TiO_2	4.11% By wt.
Unburnt Carbon	0.03% By wt
LOI (Loss on Ignition)	0.06% By wt

Experimental Methods

Batch adsorption experiments were carried out at room temperature (30^0C) by varying mixing time, adsorbent doses, initial concentration of dye and pH values on a magnetic stirrer using 250 ml screw-cap conical flasks containing 100 ml of dye solution, pH 3.5 and agitation speed of 500 rpm. The final equilibrium concentrations were measured by using UV-VIS Spectrophotometer-117 (Systronics) at 540 nm after each treatment. The percentage of the removal of dye and amount adsorbed (mg/g) was calculated by using the following relationship.

Percentage removal (%) = $100(C_0-C_e)/C_0$ (1)

Amount adsorbed (q_e) = $(C_0-C_e)/M$ (2)

Where: C_0 = Initial concentration of dye

C_e = Equilibrium or final concentration of dye (mg/l)

M = Mass of adsorbent (g/l)

RESULTS AND DISCUSSION

Effect of Mixing Time on Adsorption Equilibrium

250 ml screw-cap conical flask containing 100 ml of RR 194 dye solution with initial dye concentration (50 mg/l) and fixed amount of Fly Ash as adsorbent. The flasks were agitated on magnetic stirrer at 500 rpm and room temp (30 ^{o}C) for different time intervals. After that the effect of mixing time on the percentage removal of RR 194 dye was investigated and it was reported in table 4. The percentage removal of dye by fixed amount of Fly Ash was rapid in the beginning but after a certain time a saturation point was appeared (as shown in fig.

2) which is the equilibrium point and the graph remains constant.

Table 4: Effect of mixing time on adsorption equilibrium

mixing time (mins)	colour removal (%)
30	18
60	30
120	32
180	47
240	49
300	50
360	50
420	50

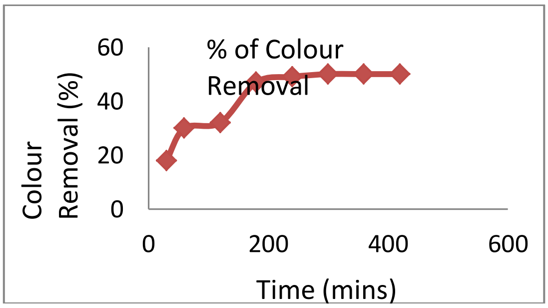

Figure 2: Effect of mixing time (mins) on dye removal. Initial dye concentration 50 mg/l ,pH=3.5, at 30°C, agitation speed 500 rpm

Effect of Adsorbent Doses on Adsorption Equilibrium

The removal of RR194 by Fly Ash at different doses for a dye concentration of 50 mg/l is already reported in table 5. Increases in adsorbent dose increased the percentage removal of dye as shown in fig.3, which is due to the increases in adsorbent surface area of the sorbent.

Table 5: Effect of adsorbent doses on adsorption equilibrium

amount of fly ah (g/l)	% of colour removal
10	30
15	47.3
20	49.5
25	51.2
30	57.4
35	57.6
40	61

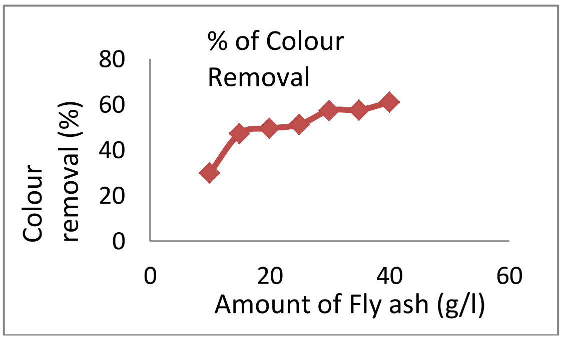

Figure 3: Effect of the adsorbent doses (Fly ash) on dye removal. Initial dye concentration 50 mg/l, pH=3.5, at 30oC, agitation speed 500 rpm

Effect of Initial Dye Concentration on Absorption Equilibrium

The effect of initial dye concentration of dye on the removal of RR194 (in terms of percentage removal) has been studied with constant dose of Fly Ash and reported in table 6. The percentage removal of dye was found to be decreased with the increase in initial dye concentration. This indicates that there exist reductions in immediate solute adsorption, owing to the lack of available active site required for the high concentration of RR194 as shown in fig. 4. The result shows that the percentage of removal of dye decreases from 96.6% to 44.08% as the concentration of dye increases from 10 mg/l to 100 mg/l.

Table 6: Effect of initial dye concentration on adsorption equilibrium

Concentration of dye (mg/l)	% of colour removal
10	96.6
20	96.5
30	86.9
40	86
50	76.3
60	66.29
70	60.74
80	56.2
90	54.8
100	44.08

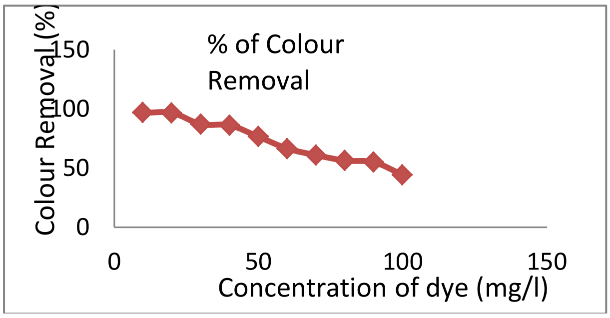

Figure 4: Effect of initial dye concentration on dye removal by constant amount of fly ash at pH=3.5, temp= 30°C, agitation speed 500 rpm

Effect of pH on Adsorption Equilibrium

The effect of pH on adsorption process is reported in table 7. The pH values ranged from 3.0 to 9.0. The adjustment of pH was done by using N/10 HCl and N/10 NaOH. It is observed that an increase in pH of the solution from 3 to 5 causes an increase in the percentage of removal of dye from 49.5 to 68.5%. Maximum removal takes place at pH 5. The adsorption of dye, however, decreases after pH 5.1 as shown in fig. 5.

Table 7: Effect of pH on adsorption equilibrium

pH	% of colour removal
3	49.5
4	60.8
5	68.2
6	50
7	42
8	47
9	42.4

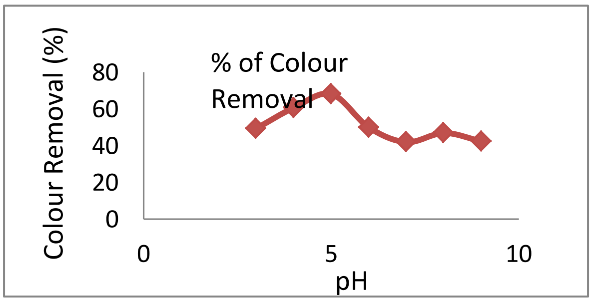

Figure 5: Effect of pH on dye removal. Initial dye concentration 50 mg/l at 30oC, agitation speed 500 rpm

Adsorption Isotherm

The adsorption of dyes can be mathematically expressed in terms of adsorption isotherms. The data obtained from equilibrium studies was analyzed according to Langmuir and Freundlich adsorption isotherm at room temperature for effluent treatment application.

Langmuir Isotherm model

Langmuir theory was based on the assumption that adsorption was a type of chemical process and the adsorbed layer was unimolecular. The theory can be represented by the following equation:

$$Ce/q_e = 1/Q_0 b + Ce/Q_0 \qquad (3)$$

Where: q_e = amount of dye adsorbed per unit mass of adsorbent (mg/g)

Ce = dye concentration at equilibrium (mg/L)

b and Q_0 = Langmuir constants

The Langmuir plot for the adsorption of the dye onto Fly Ash at room temperature is shown in fig.6. The linear plot of Ce/q_e against Ce, confirms that in the present study Langmuir isotherm modal is suitable for explaining the adsorption process. The correlation coefficient (R^2= 0.982) close to 1 (unity) and straight line with the slope $1/Q_0$ indicates that the adsorption data of RR194 on the fly ash best fitted to the Langmuir isotherm. Q_0 (mg/g) and b (mg/L) are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The values of Q_0 and b were calculated for adsorbent from intercept and slope of linear plot of Ce/q_e Vs Ce, and their values are shown in table 8.

Table 8: Langmuir and Freundlich isotherm constants for RR 194 dye on fly ash at 30°C.

Langmuir isotherm			Freundlich isotherm		
Q_0(mg/g)	b(L/mg)	R^2	n	K_f (mg/g)	R^2
4.717	0.475	0.982	3.636	0.5587	0.802

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L). The parameter is defined by:

$$R_L = 1/1+bC_0 \qquad (4)$$

Where b is Langmuir constant and C_0 is highest dye concentration (mg/L). The value of R_L indicates that the type of isotherm to be unfavourable (R_L> 1), linear (R_L=1), favourable (0<R_L< 1) or irreversible (R_L=0). The value of R_L was found to be 0.0206. This, again, confirms that the Langmuir isotherm was favourable for adsorption of RR194 on to Fly Ash under the condition used in the present study.

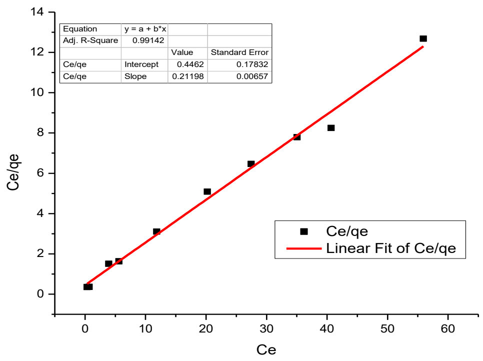

Figure 6: Langmuir adsorption isotherms for adsorption of RR194 on adsorbent fly ash

Freundlich Isotherm Modal

The empirical Freundlich equation based on sorption onto a heterogeneous surface is given as under:

$$q_e = K_f Ce^{1/n} \qquad (5)$$

K_f and n = Freundlich constants which indicate the adsorption capacity and intensity of adsorption respectively.

The linear form of Freundlich equation is given below:

$$\ln q_e = \ln K_f + 1/n \ln Ce \qquad (6)$$

The Freundlich Isotherm plot for the adsorption of the dye onto Fly Ash at room temperature is shown in fig.7. The values of K_f and 1/n are calculated from intercept and slope respectively. The values of K_f and n are shown in table.8 along with R^2 value. The slope 1/n ranging between 0 to 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. The value of 1/n below one indicates a normal Langmuir isotherm while 1/n above one indicates cooperative adsorption [4]. The result shows that RR194 is favourably adsorbed on activated Fly Ash. The Langmuir isotherm fits quite well with the experiment data (correlation coefficient R^2 =0.982).

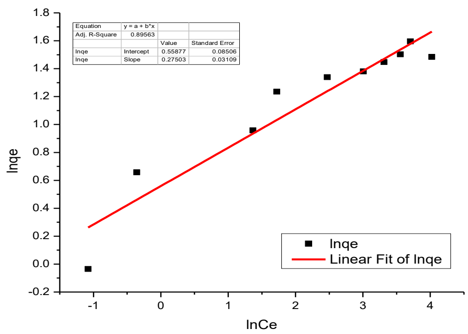

Figure 7: Freundlich adsorption isotherm for adsorption of RR194 on fly ash

CONCLUSION

In this work, the Fly Ash activated by N/2 H_2SO_4 has been used successfully as an adsorbent for the removal of Reactive Red 194 dye from the textile effluent. Experiments were performed at room temperature (30^{o}C) as a function of mixing time, initial concentration of dye, effect of adsorbent dosage, effect of pH. Based on the experimental data, Fly Ash was an effective adsorbent for the removal of RR194 from a textile effluent. Removal efficiency increased with decreasing dye concentration, maximum removal (96.60%) takes place at lower concentration (10g/l) and with increasing adsorbent dose and mixing time but after a certain point a saturation point was appeared. The result of pH shows that the adsorbent was effective in acidic medium (pH=5). This is attributed to the increasing electropositive charge of the adsorbent which favoured the adsorption of dye anions due to the electrostatic attraction.

The Langmuir and Freundlich isotherm models were used to investigate the adsorption equilibrium of adsorbent. Equilibrium data were fitted to the Langmuir and Freundlich isotherm and the equilibrium data were best described by Langmuir isotherm model. The monolayer adsorption capacity (Q_0) and adsorption energy (b) obtained from Langmuir isotherm for Fly Ash were found to be 4.717 mg/g and 0.475 L/mg, respectively.

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