International Journal of Advanced Technology in Engineering and Science www.ijates.com
Volume No.02, Issue No. 10, October 2014 ISSN (online): 2348 – 7550

ADSORPTIVE REMOVAL OF PHENOL BY COAL FLY ASH: EQUILIBRIUM AND THERMODYNAMIC STUDIES

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ABSTRACT

Fly ash utilized as a potential low cost adsorbent for the removal of phenol from wastewater. The adsorbent was characterized using various techniques such as XRD, SEM and FTIR. Batch studies involving parameters like contact time, reaction temperature; pH, adsorbent dose and adsorbate concentration were investigated. Equilibrium model analysis indicated the fitness of Langmuir isotherm model to phenol-CFA adsorption system, suggesting the monolayer adsorption of phenol onto coal fly ash.

Keywords- Coal Fly Ash, Langmuir Isotherm Model, Monolayer Adsorption, Phenol.

I. INTRODUCTION

Phenolic compounds are known to have a toxic effect on aquatic life, plant and animals. Ingestion of phenol at a concentration level of 10 to 240 mg/L for a prolonged period causes diarrhea, mouth sours, excretion of dark urine and impaired vision. Per the recommendation of world health organization the threshold concentration of phenol in potable water is 0.001 mg/L (1).This makes it necessary to use suitable method for the removal of phenol from wastewater. Among the various methods used in phenolic wastewater treatment, adsorption process is considered better due to its simplicity of design, ease of operation and convenience. Adsorption of organic compounds by activated carbon has been studied extensively (2, 3, 4,).However the high cost of adsorbent and irreversible nature of adsorption makes its use limited. Several workers used a variety of adsorbents viz. activated sludge (5), leaf litter(6) , water hyacinth ash (7), clay (8), tendu leaf (9),bentonite (10) for the removal of organic compounds from wastewater. The potential of fly ash as a natural adsorbent had been investigated by Sanjay P. Kamble et al. (11), Richa Saran et al. (12), I. J. Alinor et al. (13), Bhumica Agarwal et al. (14), B.K. Singh et al. (15), Mitali Sarkar et al.(16), J. H. Potgieter et al.(17), M. Melih Demirkan et al.(18), P. K. Sahoo et al. (19) R.K.Singh et al. (20).Their work identified the potential for removing phenol and its analogues. However, the results appeared to less comprehensive, and more practical factors should be chosen to test the effectiveness of fly ash to remove phenol from aqueous solution. In this paper, batch experiments were designed for the sorption process, and the effects of temperature, pH value, initial concentrations of phenol and fly ash dosages on adsorption were evaluated. The optimum condition was also discussed for phenol removal.

II. MATERIALS AND METHODS

Coal fly that was collected from H.E.G. Thermal Power Station, Mandideep (Bhopal) and used without any pretreatment. Phenol of Anal grade supplied by Merck, India used as an adsorbate. The stock solution was prepared in deionized water. Fresh solution was prepared on a daily basis with the initial concentration of the adsorbate calculated before the start of any experiment. The standard calibration curve of known concentrations of phenol was plotted by finding out the absorbance at the characteristic wavelength of λmax 270nm. All the samples were covered throughout the experiment to prevent photodecomposition. The equilibrium adsorption uptake and percentage removal of phenol from the aqueous solution q_e (mg/g) was determined or calculated using the following relationship:

$$\text{Amount adsorbed } q_e = \frac{(Co-Ce)V}{W} \ (\text{mgg}^{-1}) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$\%\text{ removal } q_e = \frac{100\,(Co-Ce)}{Co} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

Where C_o is initial adsorbate concentration (mg L^{-1}), Ce is equilibrium adsorbate concentration (mg L^{-1}), V is the volume of solution (L), W is the mass of adsorbent (g).

III. RESULTS AND DISCUSSIONS

3.1 Characterization Of The Adsorbent

3.1.1 XRF Analysis

The chemical composition of coal fly ash determined by X-ray fluorescence spectrometer is shown in table 1. The result shows that the mineralogy of this CFA is very rich and it is class F fly ash. The sum of SiO_2, Al_2O_3 and Fe_2O_3 content in the CFA was found to be greater than 70%, while its CaO content was lower than 5%. Minor elements within the CFA were also identified by the XRF and the results reveal that trace elements like Sc, Ni, Cu, Sr, Rb, Zr, Nb are also present.

Table 1

Constituents	Weight %	Constituents	Weight %
SiO_2	55.26	V_2O_5	0.11
Al_2O_3	22.75	BaO	0.08
Fe_2O_3	7.12	MnO	0.08
CaO	4.10	Sc_2O_3	0.05
TiO_2	2.95	SrO	0.04
K_2O	2.14	ZnO	0.04
P_2O_5	1.65	NiO	0.03
SO_3	1.58	RbO_2	0.02
Na_2O	1.23	CuO	0.02
MgO	0.63	Nb_2O	0.01
ZrO_2	0.11		
Surface area Average particle size	2892 Blaine 49 µ		

3.1.2 EDX Analysis

Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. The EDX analysis result of fly ash is represented in fig. 3.1.

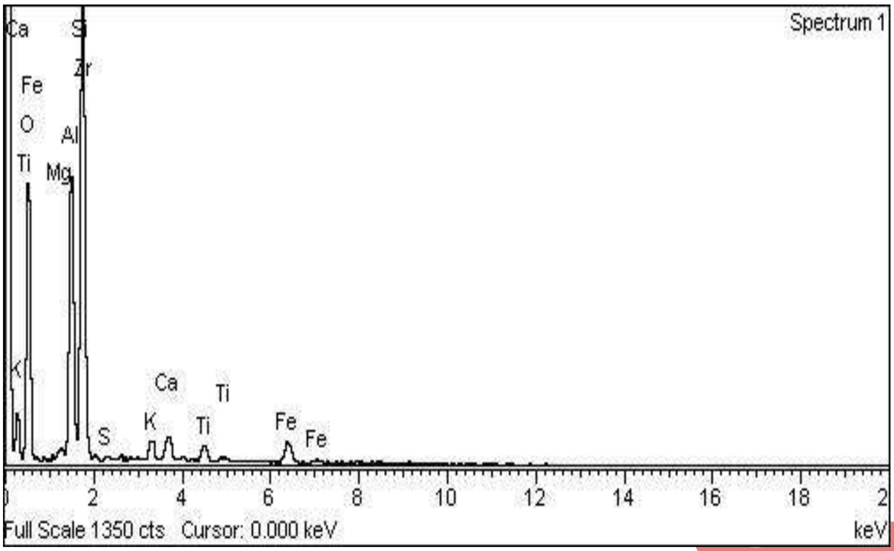

Fig. 3.1 Energy-Dispersive X-Ray Spectrum Of Fly Ash

3.1.3 XRD analysis

The identification of the mineralogical constituents and phase properties of fly ash was examined by X-ray diffracter on a model Bruker D-8 advance X-ray diffractometer and is shown in fig. 3.2.

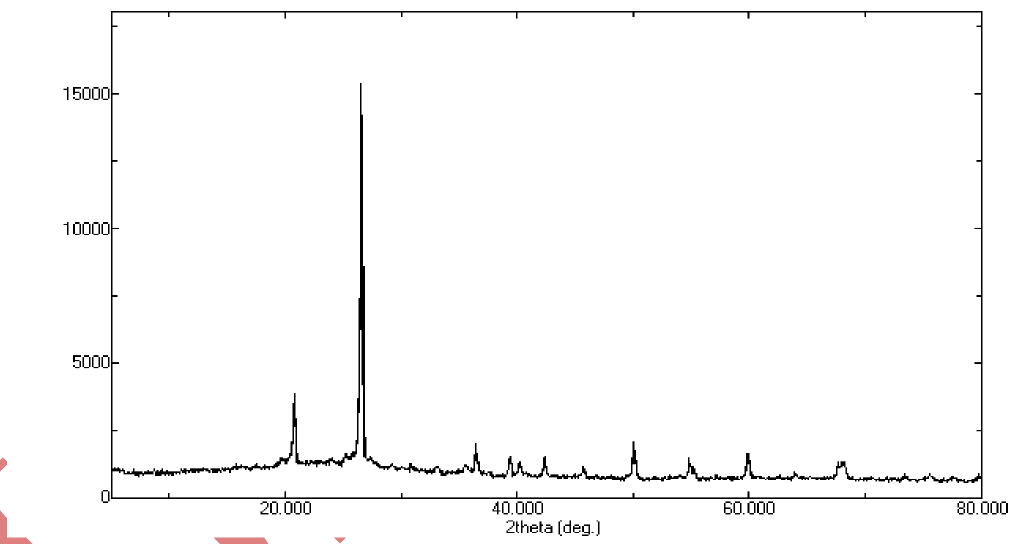

Fig. 3.2 X-Ray Diffraction Pattern Of Fly Ash

It can be observed from fig. 3.3 that the fly ash consists mostly of mullite, quartz, a small amount of hematite and calcium oxide with large characteristic peaks of quartz (SiO_2). 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.

3.1.4 SEM Analysis

SEM stands for scanning electron microscopy, which is used for studying the surface morphology of substances due to its high magnification imaging capability. The scanning electron micrograph is given in fig. 3.3.

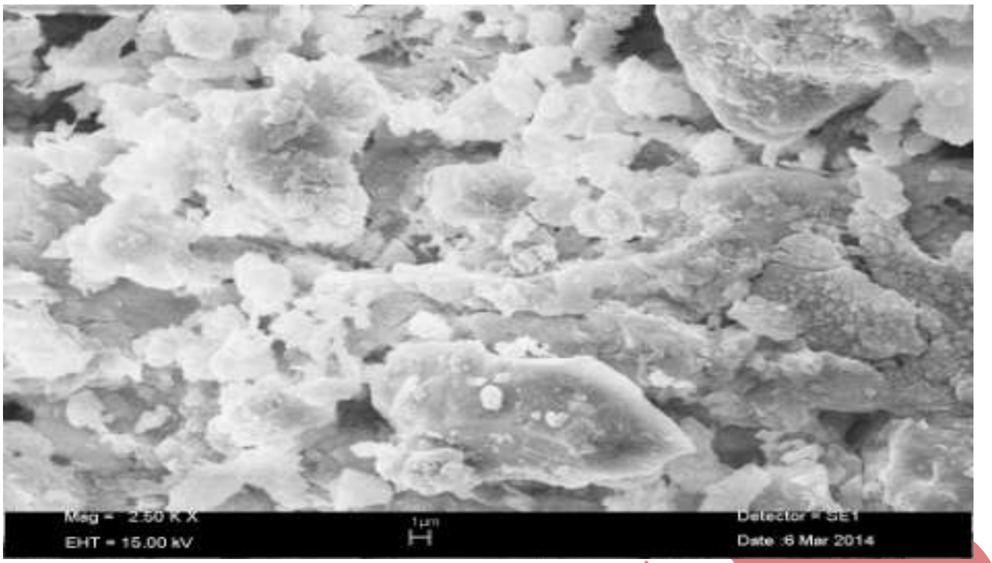

Fig. 3.3 Scanning Electron Micrograph Of Fly Ash

The image reveals that most of the particles present in the fly ash are irregular in shape and covered with relatively smooth grains of quartz.

3.1.5 FTIR Analysis

The FTIR data shows the functional groups that are on the surface of coal fly ash. The band appearing at 560 cm^{-1} is associated with octahedral aluminium present in mullite. In addition, bands appearing between 800-600 cm^{-1} are associated with tetrahedral vibrations formed which are known as secondary building units and fragments of aluminosilicate system. Band appearing at 2360 cm^{-1} could be attributed due to alkyl groups that are present in clay material of coal fly ash. Bands appearing at 800-1200 cm^{-1} and 450-550 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.

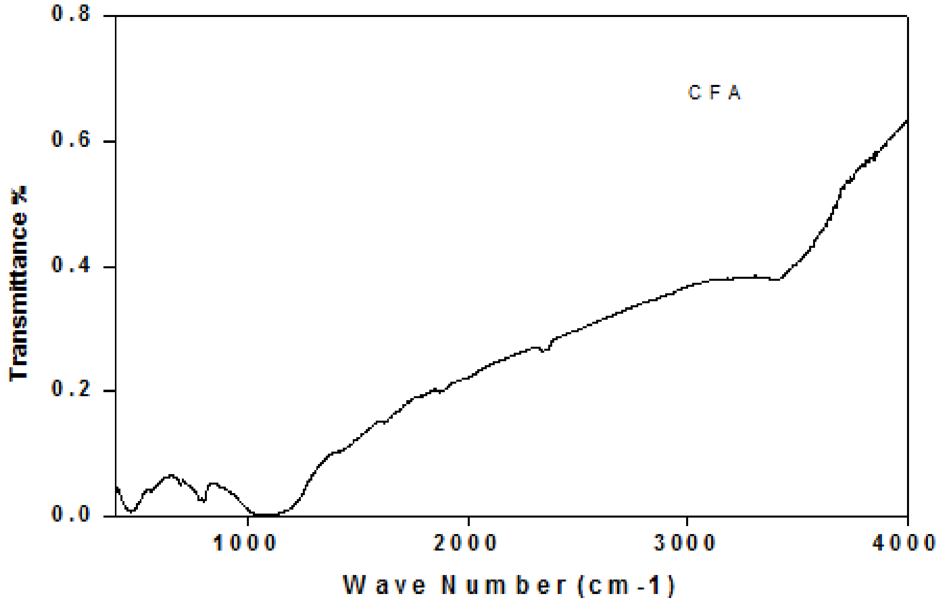

Fig. 3.4 FTIR Spectrum of CFA

3.2 Batch Studies

3.2.1 Influence Of Initial Adsorbate Concentration And Contact Time

The effect of initial phenol concentration was studied varying the phenol concentrations of 5, 10, 20 ppm. with a fixed adsorbent dose of 10 g/l at 30$\underline{+}$1^{o}C.

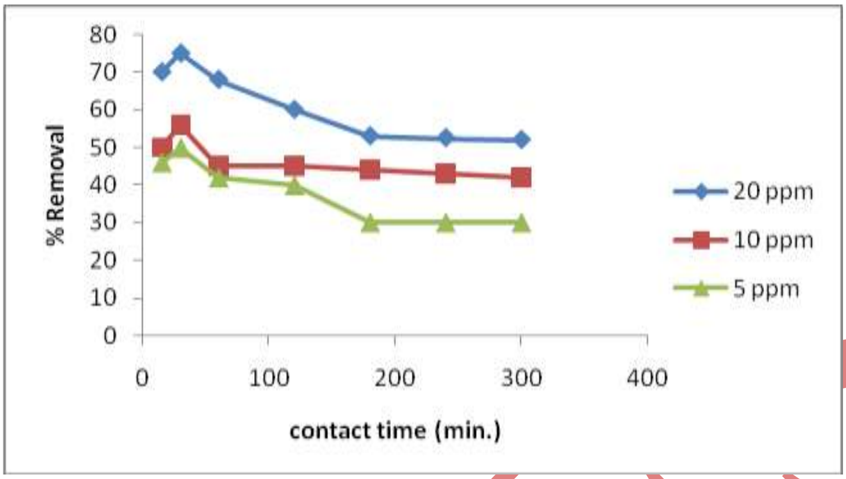

Fig. 3.5 Influence Of Initial Adsorbate Concentration And Contact Time

(Operating conditions: -pH: 6, T: 30^{o} C, C_0: 10 mg/l)

From the Fig. 3.5 it is cleared that, 75 % of the total amount of phenol uptake was found to occur in the first rapid phase (30 min) with 20 ppm phenol concentration and thereafter the adsorption rate was found to decrease. The higher adsorption rate at the initial period (first 30 min) may be due to an increased number of vacant sites on the adsorbent available at the initial stage.

3.2.2 Influence Of Temperature

The effect of temperature on the removal efficiency was investigated in the temperature of 30^{0} and 40^{0}C. The experiments were carried out with fixed adsorbent dose of 10 g/l of fly ash and pH 6.

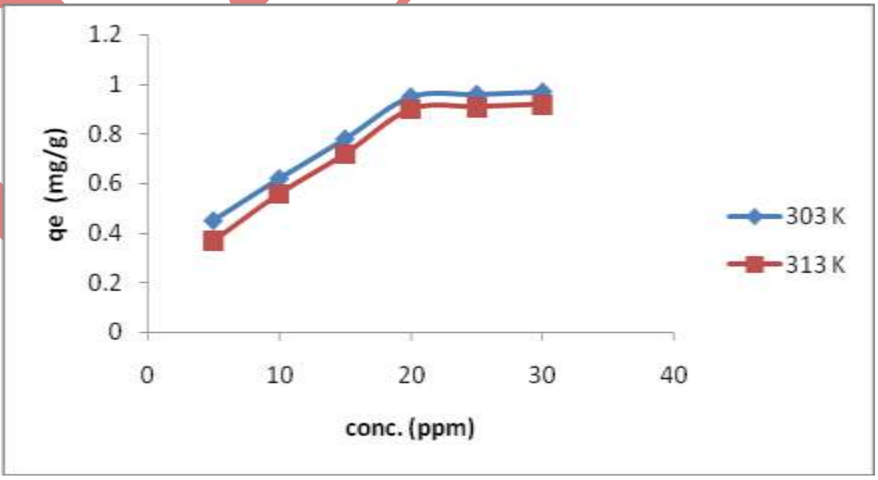

Fig. 3.6 Influence Of Temperature

(Operating conditions: - pH: 6, t: 30 min., C_0: 10 mg/l)

Results indicating that phenol uptake were favoured at lower temperature. The decrease in adsorption with the rise of temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate.

3.2.3 Influence of pH

The pH of the solution was found to influence the adsorption of the adsorbate on fly ash. The degree of adsorption of this adsorbate onto the CFA surface is primarily influenced by the surface charge on the CFA, which in turn is influenced by the solution pH. The effect of initial pH on the adsorption of phenol was also evaluated at 30 ^{o}C at different initial pH values in the range of 2–10 for initial concentrations of 20 ppm for phenol solution adjusted by adding either 0.1M HCl or 0.1M NaOH.

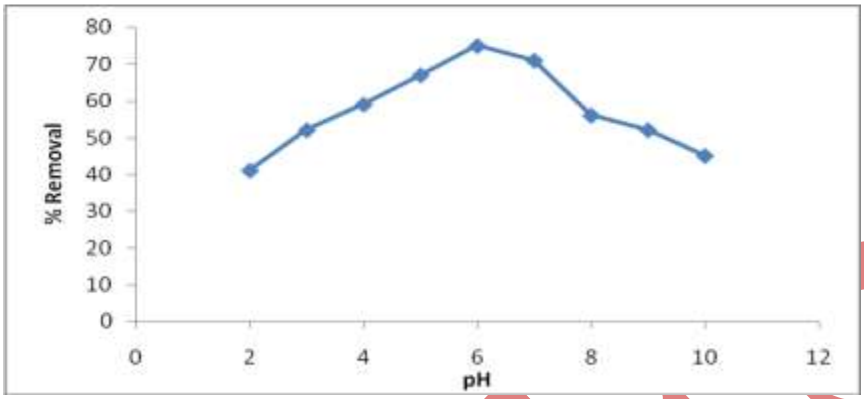

Fig. 3.7 Influence of pH

(Operating conditions: - T: 30^{o} C, t: 30 min., C_0: 10 mg/l)

The percent adsorption increased from pH 2 to 6 and decreased from pH 6 to10. The maximum amount of adsorption occurred at pH 6. The results given above suggested that adsorbed amount decreased with increasing pH value, which can be attributed to the phenol ionization to form phenolate ions and at the same time the presence of hydroxyl ions on the adsorbent prevents the uptake of phenolate ions.

3.2.4 Influence Of Adsorbent Dosage

In order to investigate the effect of mass of adsorbent on the adsorption of phenol, a series of adsorption experiments was carried out with different adsorbent dosage at an initial phenol concentration of 20 ppm. Fig. 3.8 shows the effect of adsorbent dosage on the removal of phenol.

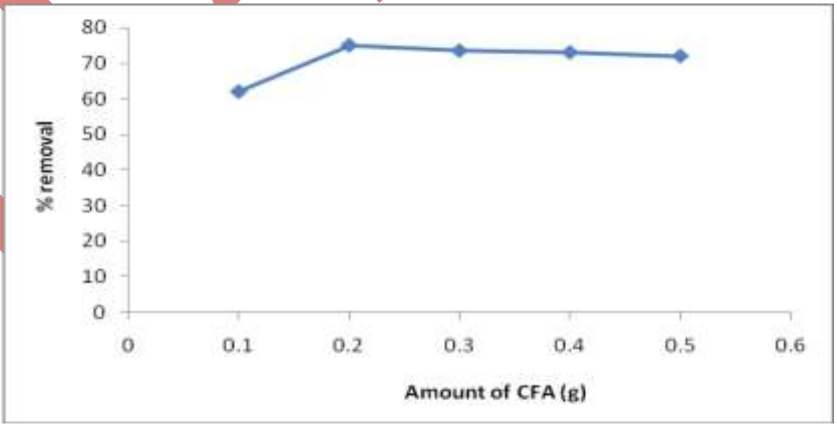

Fig. 3.8 Influence Of Adsorbent Dosage

(Operating conditions: - T: 30^{o} C, t: 30 min., pH: 6)

The percentage removal of phenol increased with the increase in adsorbent initially from 0.1 to 0.2 g. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase adsorbent dosage. With the increase in the amount of adsorbent, the sites for adsorption increased initially. But on increasing it further the adsorption efficiency is reduced. It may be due to the overcrowding of phenol molecules which prevent the diffusion through the actual adsorption sites.

3.2 Adsorption Equilibrium Study

3.2.1 Langmuir isotherm model

The most widely used isotherm equation for modeling of the adsorption data is the Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number identical site. The rearranged Langmuir isotherm equation can be described as:

$1/q_e = 1/q_m + (1/bq_m)(1/c_e)$ ………………… (3)

The Langmuir constant q_m and b can be calculated by plotting 1/ q_e versus 1/C_e. The plot of 1/ q_e vs. 1/C_e should yield a straight line.

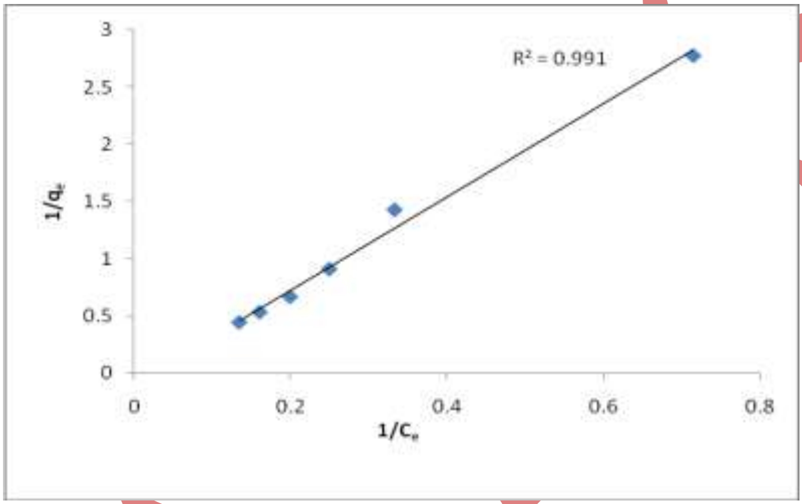

Fig. 3.9 Langmuir isotherm plot of Phenol-CFA adsorption system at 303 K

(Operating conditions: - T: 30° C, t: 30 min., pH: 6, C_0: 10 mg/l)

In the similar way Langmuir isotherm plot for Phenol-CFA adsorption system at 313 K was also made.

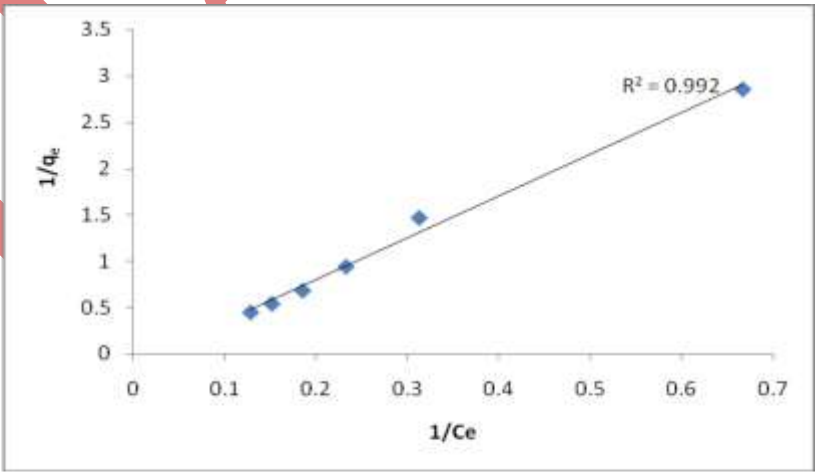

Figure: 3.10 Langmuir isotherm plot of Phenol-CFA adsorption system at 313 K

(Operating conditions: - T: 40° C, t: 30 min., pH: 6, C_0: 10 mg/l)

Various parameters calculated from these plots are tabulated below.

Table 3.2 Langmuir Isotherm Parameters Of Phenol-CFA Adsorption System

Temperature	q_m (mg/g)	b	R^2
303 K	3.3333	0.0706	0.9916
313 K	2.8571	0.0640	0.9919

3.2.2 Freundlich Isotherm Model

The linearized form of Freundlich isotherm is given below:

$$\text{Log } q_e = \log K_f + \log C_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The value of K_f and n can be calculated by plotting logQ_e versus log C_e. Where, K_f is a freundlich constant related to the adsorption capacity (mg/g) and n is an empirical constant.

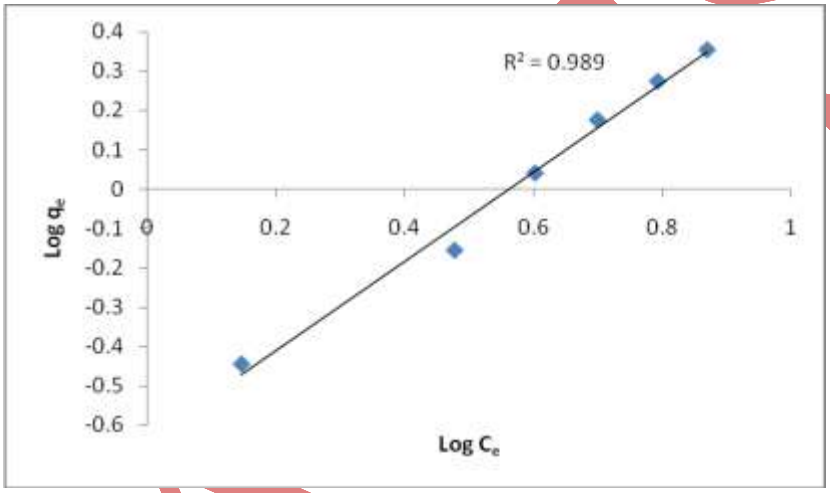

Fig. 3.11Freundlich Isotherm Plot Of Phenol-CFA Adsorption System At 303 K

(Operating conditions: - T: 30^o C, t: 30 min., pH: 6, C_0: 10 mg/l)

In the similar way Freundlich isotherm plot for Phenol-CFA adsorption system at 313 K was also made and various parameters calculated from these plots are tabulated below.

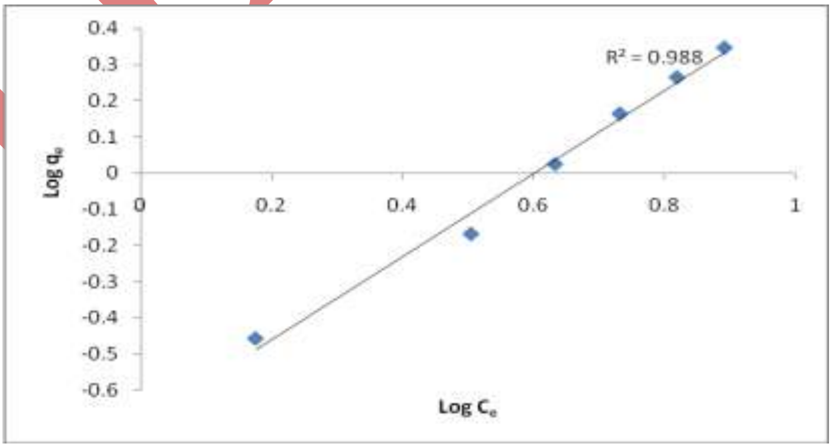

Fig. 3.12Freundlich Isotherm Plot Of Phenol-CFA Adsorption System At 313 K

(Operating conditions: - T: 40^o C, t: 30 min., pH: 6, C_0: 10 mg/l)

Table 3.3 Freundlich Isotherm Parameters Of Phenol-CFA Adsorption System

Temperature	**K_f**	**n**	**R^2**
303 K	0.2344	0.8170	0.9891
313 K	0.1995	0.7770	0.9889

It is clear from the tables 3.2 and 3.3 that the equilibrium data were very well fitted to Langmuir isotherm as compared to Freundlich isotherm. The best fit of equilibrium data in the Langmuir isotherm expression predicted the monolayer coverage of phenol onto CFA with the maximum sorption capacity as 3.3333 mg/g.

3.3 Thermodynamic Studies

The thermodynamic parameters for the adsorption of phenol were calculated by using the following equations :

$\Delta G = -RT\ln K$ ………………. (5)

$\Delta H = \Delta G + T\Delta S$ ……………… (6)

Therefore, $\ln K = -\Delta H/RT + \Delta S/R$ ………………… (7)

Where, K the equilibrium constant is defined as,

$K = C_{Ac} / C_e$ ………………… (8)

Ce is equilibrium adsorbate concentration in solution (mg L^{-1}),

C_{Ac} is the equilibrium concentration on the adsorbent (mg g^{-1}),

R is the universal gas constant and

T is the absolute temperature.

The values of thermodynamic parameters are given in Table 3.4. A perusal of data indicated that the free energy decreased with an increase in temperature thereby indicating decrease in adsorption at higher temperature and exothermic nature of the adsorption. The negative value of ΔG^0 indicated that the adsorption is favourable and spontaneous. The positive value of ΔS showed the process is associated with randomness.

Table 3.4-Thermodynamic Parameters

ΔG (**KJ/mole**)		**ΔH** (**KJ/mole**)	**ΔS** (**KJ/mole K**)	
303 K	**313 K**		**303 K**	**313 K**
-6.6787	-7.1545	-7.7538	0.003548	0.001914

IV. CONCLUSIONS

The following conclusions can be drawn from this research work:

1. Approx. 75% of phenol was adsorbed within the first thirteen minutes after which there was a slow process.
2. The pH was found to be significant factor which affects the adsorption capacity of phenol. At a pH of 6 the higher percentage adsorbate removal found.
3. The higher percentage adsorbate removal found with optimum adsorbent dose of 10 g/l.
4. Phenol adsorption capacity of fly ash was found to be decreasing with increase in temperature suggesting that the adsorption process was exothermic in nature.
5. Characterization of fly ash confirmed the rich mineral content and mesoporous texture.

6. Equilibrium model analysis indicated the fitness of Langmuir isotherm model to phenol-CFA adsorption system, suggesting a monolayer adsorption of phenol on the surface of CFA.

V. ACKNOWLEDGEMENT

Authors are grateful to MPCOST, Bhopal (MP) for financial support.

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