Adsorption as Green Technique for the Removal of Phenol from aqueous solution using Coal Flyash as Adsorbent

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Abstract

Adsorption process is widely used for removal of organic pollutants from aqueous media. As commercially available activated carbon is an efficient adsorbent, but its practical use is limited due to its high cost and complicated regeneration process. The aim of this investigation is to explore the potentiality of coal flyash as an alternative adsorbent for phenol removal from aqueous media. The coal flyash is characterized through Fourier transform infrared spectroscopy (FT-IR) which shows the presence of quartz, alumina, hematite and different mineral matters. Batch type experimental studies are performed on synthetic wastewater involving different parameters like particle size of flyash, pH effect and temperature. The experimental data are analyzed by Langmuir models in order to describe the equilibrium isotherms ($R^2 > 0.96$). The adsorption of phenol is decreased with increasing particle size and pH but increases with temperature. The study shows that coal flyash can be used as a new and effective adsorbent material for the removal of phenol from aqueous media. It was found that these low cost flyash adsorbent demonstrated good removal capability for phenol and hence can be used economically on large scale.

Keywords: Adsorption, isotherm, low cost adsorbents, Langmuir, Flyash, FT-IR.

Introduction

Phenols are organic compounds of great environmental interest. Their determination has been increasing in recent years because of their toxicity, even at low concentrations. Phenolic compounds are often derived from different manufacturing processes such as pharmaceutical, oil refineries, coke oven plants, and phenolic resin plants [1,2]. Phenolic compounds emit an unpleasant odor and flavor in portable water even at low concentration (5 μg L^{-1}) which are poisonous to aquatic life, plants and humans. Kumar et al have reported that the presence of phenols in concentrations from 10 to 240 mg L^{-1} for long periods causes mouth irritation, vision problems, diarrhoea and excretion of dark urine[3]. They are considered one of the priority pollutants by the US Environmental Protection Agency[4,5]. World Health Organization (WHO) has established the maximum permissible concentration of phenols in drinking water as 1 mg L^{-1} [6]. As a result, various studies have been conducted for the removal of phenolic compounds before being discharged to receiving sink.

The treatment of this type of wastewater involves recuperative techniques such as solvent extraction, adsorption, filtration, precipitation, ion exchange, biological treatment and destructive techniques such as ozonation and oxidation[2,7]. The shortcomings of most of these techniques are high investment along with maintenance costs, secondary pollution (generation of toxic sludge, etc.) and complicated treatment procedure. On the other hand physicochemical treatments such as coagulation/flocculation processes are generally found to be unable to remove some kind of pollutants. As advanced oxidation process can be effective for the removal of emerging compounds, these processes can lead to the formation of oxidation intermediates which are mostly unknown at this stage.

Conversely in adsorption processes, there is no any addition of any undesirable by-products and so it is found to be superior to other techniques for wastewater treatment in terms of simplicity of design, easy as well as economic in operation and insensitivity towards toxic substances[1]. So Adsorption as green technology using activated carbon is currently being utilized in a large scale for the removal of pollutants from gaseous and liquid phases. Due to the high cost of activated carbon, there is a need to look for cheaper material especially natural thing that are easily available e.g. clay[8]. The main disadvantages associated with activated carbon are the high regeneration cost, intraparticle resistance in adsorption process and poor mechanical strength[3, 9].

Recently, adsorption has attracted considerable interest especially from low-cost industrial wastes and natural resources for the removal of phenol and phenolic compounds. These wastes require no any pretreatment or little processing to increase their adsorption capacity. Various industrial wastes and agricultural materials such as paper mill sludge, coal, dried sewage waste, water hyacinth ash, green macro alga, rice husk ash and coal flyash have been explored for their technical visibility to remove phenols [5, 9].

In this study, we report the removal of phenol from aqueous media using coal flyash. The coal flyash is characterized through FT-IR spectroscopic studies. The effect of various factors such as different particle size, initial pH of adsorbate solution and temperature are investigated under batch type equilibrium study.

Equilibrium adsorption data are fitted well to Langmuir adsorption isotherm model.

Material and Methods

Preparation and application of Adsorbent: Flyash is obtained from Thermal Power Station, Chachai, Anooppur, Shahdol (M.P.) India. The fly ash is sieved through standard test sieves having geometrical mean size 150, 106, 45µm respectively. The different fraction of flyash dried for 2 hours at 110^0C in an electric oven and stored in a desiccator for use.

Characterization of Coal Flyash: The chemical constituents of flyash are determined by Indian Standard methods[10] along with other characteristics such as loss on ignition (LOI) at 800^0C, specific gravity, surface area and porosity and are shown in table-1. The chemical constituents of different fractions of flyash are also determined by Indian Standard methods[10] and are shown in table-2. The result shows that silica and alumina are the major constituents of flyash. The chemical analysis of flyash indicates that the sample consists of mullite. ($Al_6Si_2O_{13}$), quartz (SiO_2), magnetite (Fe_3O_4), anhydrite ($CaSO_4$), hematite (Fe_2O_3), lime (CaO) as the major phase. The occurrence of the above minerals has been confirmed by FTIR analysis. The transmission FT-IR spectra are then recorded between 400 and 4000cm-1 as KBr pellet using a Perkin Elmer to determine the type of functional groups present in the flyash sample.

Table-1
Characteristics of flyash

Element as oxide	Weight %
SiO_2	59.54
Al_2O_3	27.20
Fe_2O_3	4.87
CaO	2.91
MgO	0.40
K_2O+Na_2O	1.00
LOI (800 0 C)	12.00
Specific gravity	1.80
Surface Area	$7000 – 9000 \ cm^2$
Porosity	0.34 - 0.62

Table–2
Chemical analysis of Fraction of Flyash Chemical Composition (Percentage by weight)

Particle Size Um	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LOI 800^0C
150 µm	59.54	27.20	4.87	2.91	0.40	12
106 µm	67.00	30.00	6.10	3.80	1.10	08
45 µm	77.75	36.00	6.00	4.00	1.50	4.09

Adsorbate: Stock solution is prepared by dissolving 1.0 g of phenol in 1.0 L double distilled water. The stock solution is then suitably diluted and used for adsorption experiments. The concentration of phenol is determined through UV-VIS spectrophotometer (Shimadzu Model UV-1601) at wavelength of 270 nm.

Adsorption experiments: Batch type adsorption isotherm experiments are performed by agitating 1.0 g. of flyash with 35 ml of various concentrations of the phenol solution in 100 cm^3 conical glass stoppard flasks in a temperature controlled shaking thermostat at different particle size (150, 106, 45µm), pH values (2.0, 4.0, 6.5, 8.0 and 10.0) and desired temperatures (30, 40,500C) for two hours and left overnight to reach equilibrium. Agitation was made for 2 h at constant oscillation of 65 strokes/minute. After reaching equilibrium, the samples are centrifuged. The supernatant liquid is analyzed for phenol using UV-VIS spectrophotometer (Shimadzu Model UV-1601) by monitoring the absorbance changes at a maximum wavelength of 270 nm. Phenol solution is buffered at desired pH value (2.0, 4.0, 6.5, 8.0, and 10.0) with 0.05M phosphate buffer to stabilize the pH. Adsorption isotherms data are obtained by allowing the adsorbent to remain in contact with the solution for overnight time for attaining equilibrium.

Results and Discussion

Characterization of Adsorbent: The FT-IR technique is an important tool to identify the characteristic functional groups on the adsorbent surface. The FT-IR spectra of one of the coal flyash sample of size 150 µm are shown in figure-1.

SiO-stretching vibrations are observed at 664.0 showing the presence of quartz in the sample[11]. The vibrations observed at 3577.5 and 1111.4 are due to the presence of Kaolinite[11]. The band 3577.5, 1604.7, 1111.4, 795.1 indicate the possibility of the presence of illite[11]. The band at 664.0.cm-1 shows the possibilities for the presence of calcite [11].

Equilibrium studies: There are a number of models that have been reported in literature to show equilibrium relationships between adsorbent and adsorbate. The Freundlich and Langmuir models are the most frequently employed models. In this work, Langmuir model is used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentrations. The linear form of the Langmuir isotherm is given by the relation:

$$C_e / q_e = 1/ Q_0b + C_e / Q_0 \qquad (1)$$

where, q_e is the amount adsorbed at equilibrium (mg g^{-1}), Q_0 (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants related to the maximum adsorption and energy of adsorption respectively. The plots of C_e / q_e vs. C_e at different conditions are found to be linear indicating the applicability of the Langmuir model. The statistical significance of the correlation coefficient (R^2) for the plot of C_e / q_e vs. C_e is the criteria for testing the fitting of the data to Langmuir isotherm model. The parameters Q_o and b have been calculated from linear plots shown in figure-3, 5 and7 and the results are represented in tables-3 to 5. The best fit of equilibrium

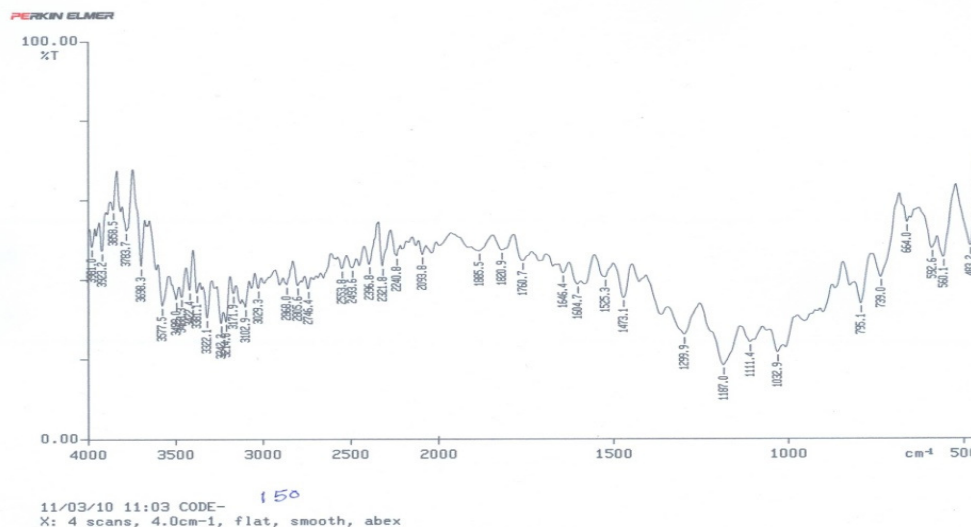data in the Langmuir isotherm model predicts the monolayer coverage of phenol on coal flyash.

Figure-1
FT-IR spectra of one of the coal flyash sample of size 150 µm

Table–3
Adsorption Isotherm Parameter for different particle size of flyash Conditions: pH 6.5; Temperature 30⁰C

Adsorbate	Particle Size of Adsorbent (µm)	Langmuir Parameters				R^2
		Q_o (mg g^{-1})	Q_o (m mol g^{-1}) x 10^{-2}	b (L mg^{-1})	b (L mol^{-1}) x 10^3	
Phenol	150	3.509	3.73	4.0299	1.90	0.998
	106	4.219	3.97	2.4979	2.12	0.999
	45	5.464	5.01	1.7317	2.17	0.998

Table–4
Adsorption Isotherm Parameter at different pH values. Conditions: Size 150µm; and Temperature 30⁰C

Adsorbate	pH	Langmuir Parameters				R^2
		Q_o (mg g^{-1})	Q_o (m mol g^{-1}) x 10^{-2}	b (L mg^{-1})	b (L mol^{-1}) x 10^3	
Phenol	2.0	4.329	4.43	2.9799	2.16	0.998
	4.0	4.000	4.07	3.7825	2.09	0.998
	6.5	3.509	3.73	4.0299	1.90	0.998
	8.0	3.145	3.34	5.2951	1.80	0.995
	10.0	2.725	2.90	8.9144	1.42	0.998

Effect of particle size of Adsorbent: Such parameters determine the capacity of adsorbent -adsorbate equilibrium system for a given phenol concentration. The chemical analysis data for CFA listed in Table -2 show the presence of material matter like aluminosiliceous and oxides of aluminium and silicon together with other minor constituents. The data also show that the amounts of alumina and silica as the major constituents are increased as the particle size decreased. The silica and alumina contents of coal flyash play a major role in the adsorption of phenol. The phenol uptake per unit mass is increased with the decrease in particle size of adsorbent as shown in figure-2. The reason for this trend may be attributed to the fact that there is strong chemical bonding between lone pair of electron present on the -OH group in the phenol and the central ion of silicate (Si+4) as well as the weakly acidic alumina surface of CFA. The surface area is also increased as the particle size decreased and so adsorption increased. Hence, in addition to the increase in alumina and silica content with decreasing particle size, the increase in the specific surface area also contribute to the observed enhanced adsorption of phenol onto the coal flyash fraction containing the smallest particles. As size of coal flyash decreases, amount of major constituents i.e. alumina and silica increases and so amount of adsorption increases and therefore adsorption capacity,Q_0 as well as adsorption energy, b determined from linear plot of figure-3 and are reported Intable-3 varies as Q_0, b (45 µm) > Q_0, b (100µm)

> Q_0, b (150µm) Similar results are reported by different authors [12, 13].
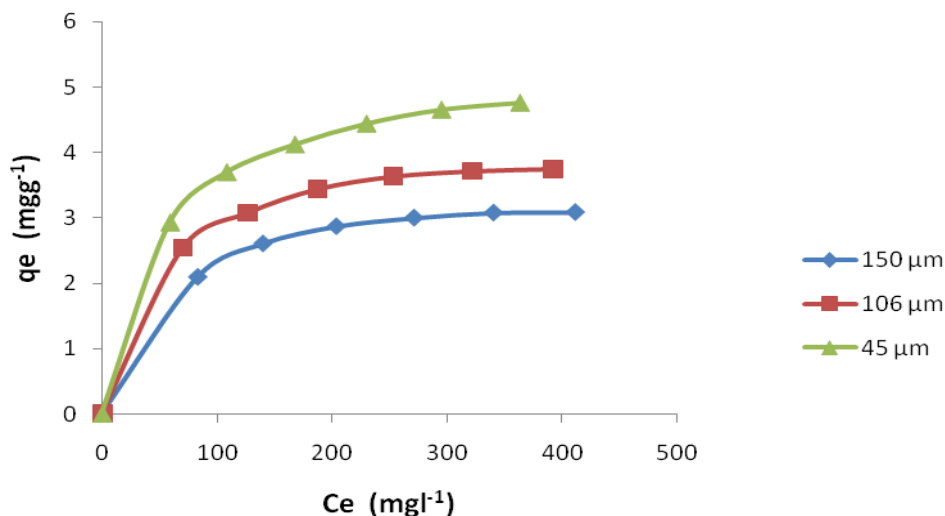

Figure-2
Adsorption Isotherm for phenol on flyash. condition :Different Size; Temperature 30°c; pH 6.5
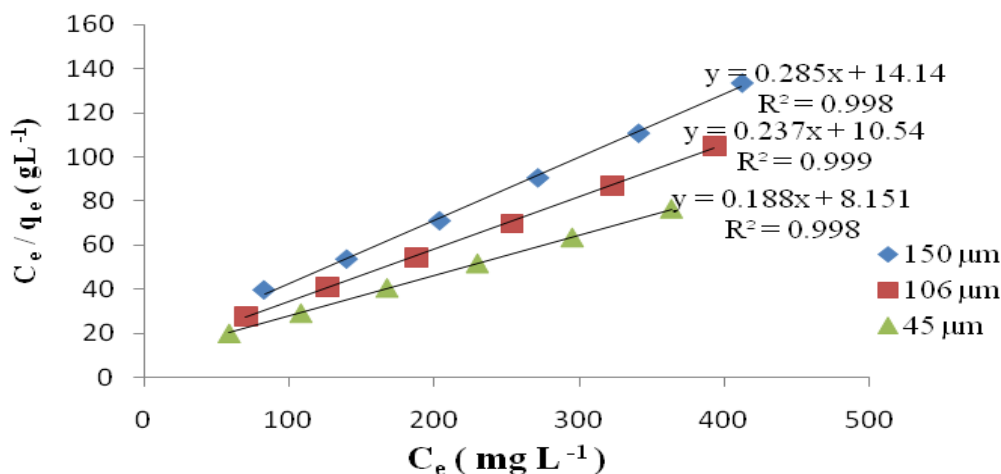

Figure-3
Langmuir plot for the adsorption of phenol on flyash: pH 6.5; Temperature 30°c .

Effect of pH of Adsorbate: The adsorption capacity is affected mostly by the pH of adsorbate solution. The pH of the solution may affect the surface charge of the adsorbent as well as degree of ionization of the adsorbate species responsible to change in equilibrium characteristics of the adsorption process. Thus, the pH value of the phenol solution imparts a significant role in the entire adsorption process. Any oxide surface creates a charge either positive or negative on its surface. The surface of coal flyash would be protonated at low pH values and hence strong electrostatic forces of attraction with the negatively charged adorbate phenoxide ion.

Adsorption at higher pH would be less due to repulsion between negatively charged surface and phenoxideion[14] .The effect of pH

on the adsorption of phenol can be shown in figure-4. Generally, the adsorbed amount decreases with increasing pH value. Competition occurs between the OH^- ions and the phenol molecules for adsorption sites. Thus, the removal capacity parameters, Q_0, as well as adsorption energy, b calculated from linear plot of figure- 5 at different pH values which is reported in table-4 varies as follows:

pH 2.0 > pH 4.0 > pH 6.5 > pH 8.0 > pH 10

Similar trends have been reported for the biosorption of phenol by activated carbon, water hyacinth ash, bagasse ash and wood charcoal, activated carbon from tobacco residues[5, 14-16].
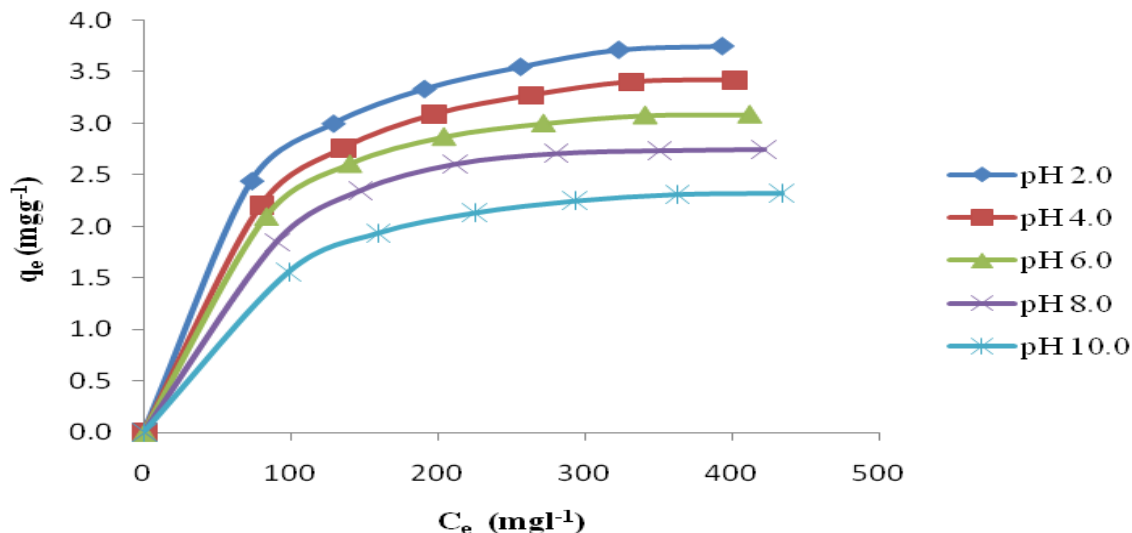
Figure-4
Adsorption Isotherm for phenol on flyash. condition :Different pH ; Particle size 150 µm; Temperature 30°C
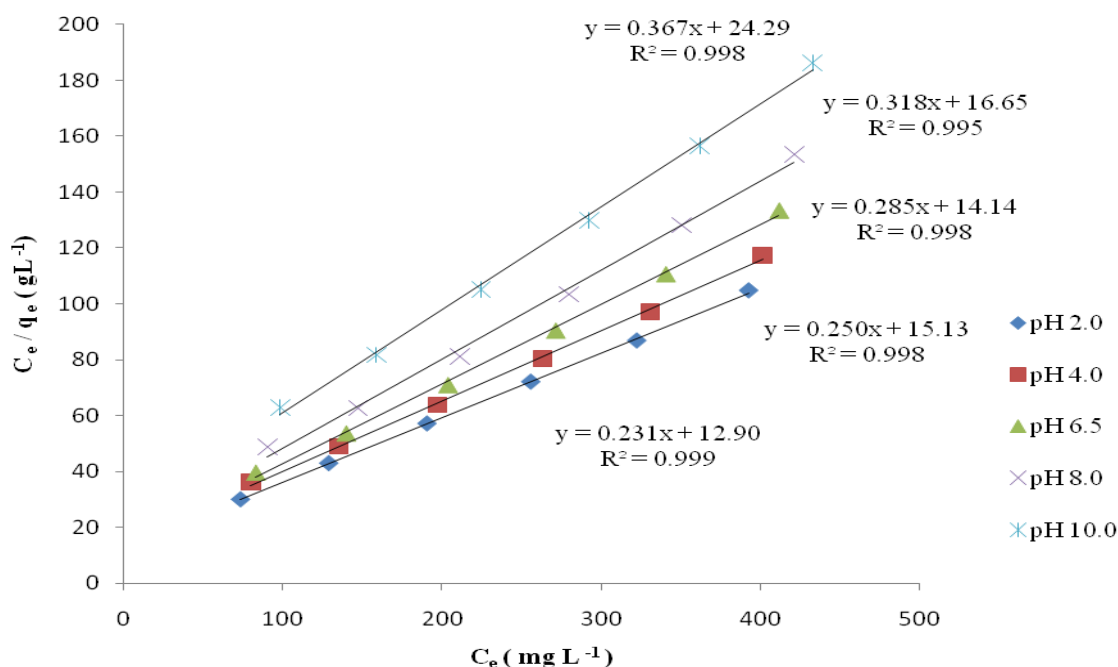

Figure-5
Langmuir plot for the adsorption of phenol on flyash. Particle size 150 µm; Temperature 30°C

Table–5
Adsorption Isotherm Parameter at different Temperatures. Conditions: pH 6.5 and Size 150 µm.

Adsorbate	Temperature (^{0}C)	Langmuir Parameters				
		Q_o (mg g^{-1})	Q_o (m mol g^{-1}) x 10^{-2}	b (L mg^{-1})	b (L mol^{-1}) x 10^3	R^2
Phenol	30$\pm$1	3.509	3.73	4.0299	1.90	0.998
	40$\pm$1	4.016	4.27	2.8684	2.03	0.999
	50$\pm$1	4.425	4.70	1.9662	2.45	0.999

Effect of temperature: To know the effect of temperature on the adsorption of phenols, experiments are performed at different temperature. The adsorbed amount of of phenol increases by increasing temperature as shown in Figure-6 varies as 30^0 C> 40° C > 50°C showing the process to be endothermic. Thus the adsorption parameters Q_0 and b calculated from linear plot of figure-7 for coal flyash at different temperature reported in table -5 varies as follows: Q_o, b (50°C) > Q_o, b (40°C) > Q_o, b (30°C)

The increase of adsorption parameters Q_0 and b with increase in temperature indicating about increase of active surface centre available for adsorption process[17]. However, the net increase would depend upon the nature of the solute. This suggests that the adsorption of phenol on coal flyash involves a chemical process.

The change of standard free energy, ΔG^o, standard enthalpy, ΔH^o and standard entropy, ΔS^o are calculated using the following equation [18]

$$\Delta G^0 = -RT \ln K \qquad (2)$$
$$\Delta H^0 = RT_1T_2 / (T_2-T_1) \ln (K_2/K_1) \qquad (3)$$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0)/ T \qquad (4)$$

Where K is known as equilibrium adsorption constant which represented as the product of the Langmuir constants,Q_o and adsorption energy, b[19]. K, K_1 and K_2 are equilibrium adsorption constant at temperature T, T_1 and T_2 respectively and R is the gas constant. The calculated thermodynamic parameters on the basis of above three equations are summarized in table-6. Positive values of ΔH^o suggests the endothermic nature of the adsorption and the negative values of ΔG^o indicate the spontaneous nature of the adsorption process. The positive value of ΔS^o shows the increased randomness of the solid/solution interface during the adsorption of phenol on coal flyash. This can be explained by the fact that each molecule of adsorbate has to displace more than one molecule of solvent. The net result corresponds to an endothermic process. This fact is also confirmed by the values of ΔS^0. The positive value of ΔS^o also shows affinity of adsorbent for phenol. The enhancement of adsorption at higher temperatures may be also due to the enlargement of pore size and or activation of the adsorbent surfaces[20].
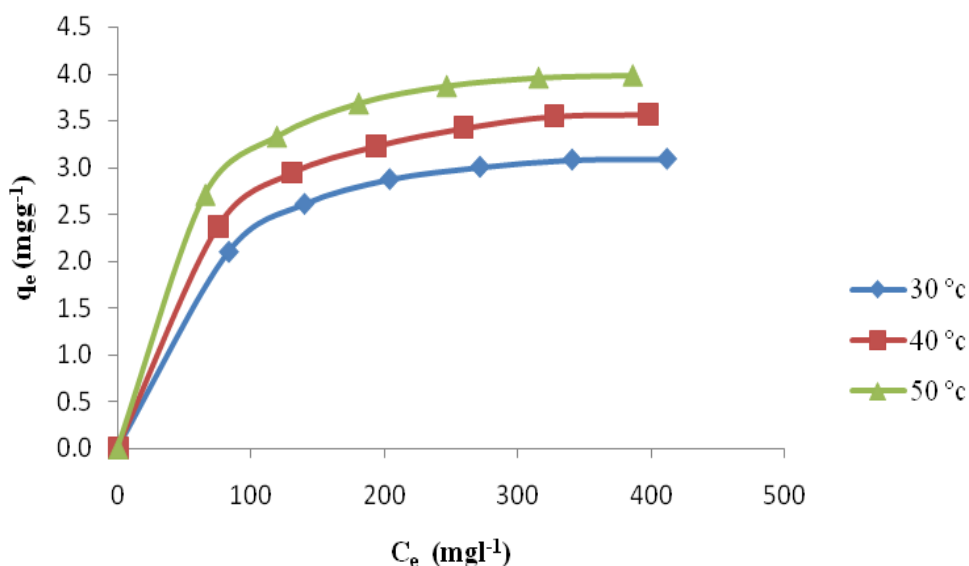

Figure-6
Adsorption Isotherm for phenol on flyash. condition: Different Tempearature; Particle size 150 µm; pH 6.5

Table–6
Thermodynamic Parameter at different Temperatures Conditions: pH 6.5 and Size 150µm.

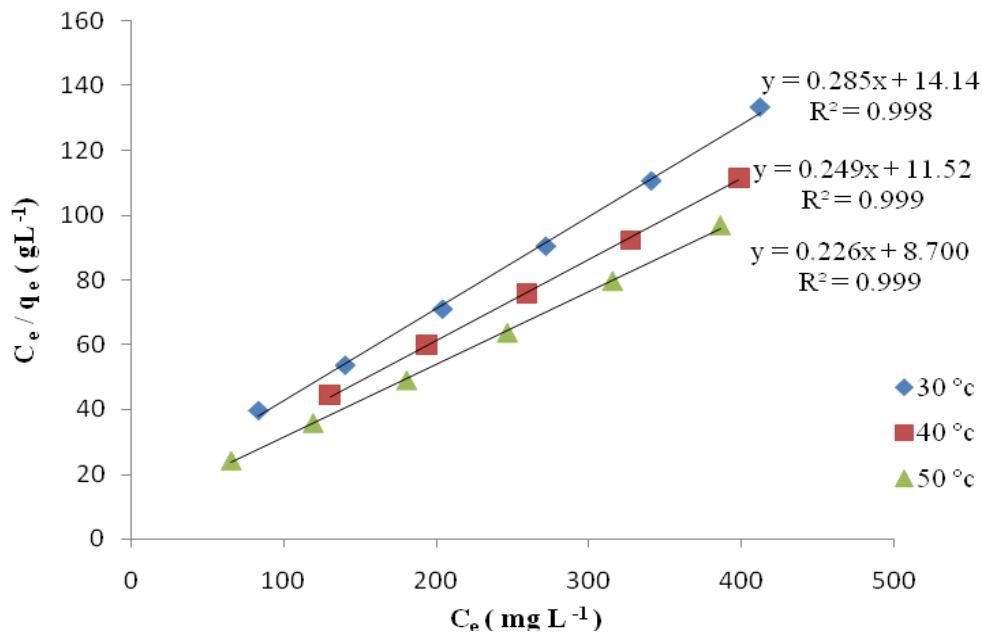| Adsorbate	Temperature (^{0}C)	K	Langmuir Parameters		
			ΔG^o (k cal mol^{-1})	ΔS^o (cal mol^{-1})	ΔH^o (k cal mol^{-1})
Phenol	30	70.87	- 2.5563	20.9168	3.7815
	40	86.68	- 2.7654	26.9157	5.6592
	50	115.15	- 3.0354	-------	-------

Figure-7
Langmuir plot for the adsorption of phenol on flyash. Particle size 150 µm; pH 6.5

Conclusions

The present investigation reports batch type adsorption studies for the removal of phenol from aqueous solution using coal flyash. Equilibrium adsorption data fitted very well to Langmuir model confirming monolayer coverage of phenol onto coal flyash. It can be concluded that some industrial waste by-products can be used as efficient and alternative adsorbents especially for the adsorption of organics due to readily available, economic and easy handling. Increasing temperature and decreasing particle size and pH increases the adsorption parameters of coal flyash for phenol .Such type of equilibrium adsorption isotherm studies are helpful in designing a treatment plant for phenolic effluents where continuous removal or recovery can be achieved on a large scale.

Acknowledgements

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