



# Adsorptive Removal of Phenols from aqueous solution by Flyash- Kinetics and Equilibrium Study

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## Abstract

The potentiality of low cost abundantly available material with good adsorption properties for removing phenols is investigated. The adsorbent is characterized using a number of experimental approaches like chemical analysis, XRF, XRD, FTIR and SEM /EDS. Chlorophenols i.e. *o*-chlorophenol (OCL), *m*-chlorophenol (MCL) *p*-chlorophenol (PCL) including phenol (PHL) are selected for the studies. The effect of various factors like adsorbent particle size, pH, phenols concentration and temperature on the adsorption *p* are investigated. The removals of different phenols are increased with decreasing adsorbent particle size, pH and increasing concentration and temperature. The adsorption of the chlorophenols and phenols studied followed first-order rate kinetics. Langmuir adsorption isotherm constants are calculated and it is seen that the adsorption data for phenols onto flyash fitted the Langmuir model well. Thermodynamic studies are also undertaken and the values of the various parameters such as standard free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) are calculated.

**Keywords:** Flyash, adsorption, phenols, langmuir isotherm model, kinetics, thermodynamic parameters, low cost adsorbent.

## Introduction

Phenols are common raw materials for manufacturing for a large number of chemical products like petrochemicals, plastics, pesticides, pharmaceuticals, dyes etc. Apart from this, these are also used to produce phenolic, epoxy and polyamide resins<sup>1</sup>. Among them, chlorophenols are an important class of aromatic pollutants in industrial wastewaters and belong to a group of common environmental contaminants<sup>2</sup>. Chlorophenols are found in the environment due to chlorination of drinking water in municipal water treatment, chlorine bleaching in numerous industries, discharge from a range of incineration processes as well as as common constituents of herbicides and pesticides on agricultural land<sup>3</sup>. So United States Environmental Protection Agency (EPA) has classified phenols as priority pollutants<sup>4</sup> due to its toxicity and adverse effect on human beings. Chlorophenols are used mostly in the manufacture of fungicides, herbicides, insecticides, pharmaceuticals, preservatives, glue, paint, fibers, leather as well as in various chemical synthesis<sup>5</sup>. Phenols are the priority contaminants of major environmental concern due to its high toxicity, carcinogenicity and poor biodegradability. Therefore it is very essential to develop efficient and effective processes for the removal of these compounds from wastewaters<sup>6</sup>. Various attempts are made in this respect like physical, chemical and biological processes for the removal of phenols from wastewater. Adsorption, chemical oxidation, precipitation, distillation, solvent extraction, ion exchange, membrane processes, reverse osmosis, etc as a traditional methods have been mostly used for removal of phenols from

aqueous solutions<sup>7-9</sup>. Adsorption as removal of phenols is the most effective and efficient method due to high efficiency, easy handling, high selectivity, lower operating cost, easy regeneration of adsorbent and minimized production of chemical or biological sludge<sup>8</sup>. Adsorption phenomena are affected strongly by the surface morphology as well as chemistry of the adsorbent. So various adsorbents like activated carbon, red mud, rubber seed coat and many more have been used for removal of phenolic compounds<sup>10-13</sup>. Among them, activated carbon is mostly used for removal of organic compounds from industrial effluents due to its high removal efficiency. But due to its high cost, it is not applicable to industrial effluents containing low concentrations of contaminants<sup>14-16</sup>. Hence, many more cheap materials have been tested for removal of organic compounds from water and wastewater. Recently much attention has been focused on the utilization of flyash including peat, wheat shells, wood sawdust, activated sludge, zeolite etc. for the removal of organics from water and wastewater<sup>17-19</sup>. The potentiality of flyash as a natural adsorbent has been investigated by various authors<sup>20-23</sup>. In this study, flyash is used as a low cost adsorbent to remove phenol, 2-Chlorophenol, 3-Chlorophenol and 4-Chlorophenol as a target pollutant from aqueous solution. The aim of this research is to study application of flyash for removal of phenol, 2-Chlorophenol, and 3-Chlorophenol and 4-chlorophenol from aqueous solutions using batch type kinetic as well as equilibrium experiments under different conditions such as particle size, pH, concentration and temperature.

## Material and Methods

**Adsorbent and its Characterization:** Flyash is obtained from Thermal Power Station, Chachai, Anoopur, Shahdol (M.P.) India. The material is sieved through standard test sieves having geometrical mean particle diameters of 150, 106 and 45  $\mu\text{m}$  respectively. The different fractions of flyash are then dried at 110°C for 2h in an electric oven and stored in desiccators without any pretreatment for subsequent use. The chemical constituents of the flyash are determined using Indian standard methods<sup>24</sup> along with other characteristics such as the loss on ignition (LOI) at 800°C, specific gravity, surface area (using a Quantasorb surface area analyzer, Quantachrome, Boynton Beach, FL, USA) and porosity (using a mercury porosimeter). These are all listed in table-1. The chemical compositions of the different fractions of flyash are also determined using Indian standard methods<sup>24</sup> and are listed in table-2.

Flyash are characterized by a number of experimental approaches like XRF, XRD, SEM/EDS and FTIR in order to investigate all the relevant features<sup>25</sup>. The chemical composition of different fractions of flyash are confirmed by XRF analysis (PAN Analytical, Model-PW 2404) and given in table-3. X-ray diffraction (XRD) is carried out on Philips PW1710 automatic X-ray diffractometer with Cu-K $\alpha$  radiation with a scanning speed of 10° min<sup>-1</sup>. Different fractions of flyash samples are subjected to Scanning Electron Microscopy on FEG- SEM (Model- JEOL JSM 7600F) coupled with Energy Dispersive X-Ray Spectroscopy (EDS) having XMAX 80 mm 2 as detector in order to investigate the morphology and chemical composition of the samples. The flyash fractions is analyzed with Fourier transform infrared spectroscopy (FTIR) using Perkin Elmer 1800 model instrument in the range 450– 4000 cm<sup>-1</sup> as potassium bromide pellet .

**Adsorbate:** Phenol (PHL), o-chlorophenol (OCP), m-chlorophenol (MC P) and p-chlorophenol (PC P) (A.R. grade) are selected for this study because they represent the most common pollutants and are readily analyzed using UV-VIS spectrophotometer (Shimadzu Model UV-1601) at wavelength of 270,274,280 and also 280 nm. Standard solutions of these phenols (500 mg/dm<sup>3</sup>) are prepared by taking appropriate quantities and dissolving them in a minimum volume of acetone. Portions of these solutions are then diluted with distilled water to give the test samples.

**Batch experiments: Kinetic Studies:** The adsorption kinetics is studied using batch experiments. Thus, 25 cm<sup>3</sup> of a given phenols at a known concentration is placed in a 100-ml conical glass-stoppered flask together with 1.0 g flyash and the flask placed in a thermostatic shaker. Again, various particle sizes (150  $\mu\text{m}$ , 106  $\mu\text{m}$ , 45  $\mu\text{m}$ ), pH values (2.0, 4.0, 6.5, 8.0, 10), concentrations (500, 350, 250 mg/dm<sup>3</sup>) and temperatures (30°C, 40°C, 50°C) are employed. However, in this case samples are taken after pre-determined intervals of time and their concentrations determined by means of a spectrophotometer

(UV-VIS spectrophotometer (Shimadzu Model UV-1601) at a wavelength of 270,274,280 and also 280 nm corresponding to maximum absorbance.

**Equilibrium Studies:** Batch adsorption experiments for determining equilibrium adsorption isotherms are also carried out by agitating 1.0 g of the desired grade of flyash with 35 cm<sup>3</sup> of a chosen concentration of a given phenols. Solutions are transferred in 100-ml conical glass-stoppered flasks and maintained in a temperature-controlled shaking thermostat for 120 min. (the time required for attaining equilibrium between the adsorbed phenols and that remaining in solution). Experiments are performed using different particle sizes (150  $\mu\text{m}$ , 100  $\mu\text{m}$  and 45  $\mu\text{m}$ ), pH values (2.0, 4.0, 6.5, 8.0, 10.0) and temperatures (30°C, 40°C, 50°C). The pH of the initial solution was adjusted with 0.1N HNO<sub>3</sub> or 0.1N NaOH solution using pH meter. At equilibrium, samples are taken from the flasks, filtered through a filter paper and centrifuged. The concentrations of the residual different phenols are determined as described above.

## Results and Discussion

**Characterization of Flyash: XRD analysis:** The diffractogram for one of the fraction of flyash (150  $\mu\text{m}$ ) is shown in figure-1. The XRD analysis of flyash sample indicates the presence of quartz, alumina, hematite and illite etc. It can be observed from figure-1 that the flyash consists mostly of mullite, quartz, alumina, a small amount of hematite and calcium oxide with intense characteristic peaks of quartz (SiO<sub>2</sub>). The intensity of quartz is very strong with mullite and dense glassy surface layer. It can be seen from the diffractogram of flyash sample that components are mainly present in their oxide form. These results are similar to that reported for a flyash investigated by Dwivedi et al<sup>25</sup>.

**SEM/EDS Analysis:** SEM stands for scanning electron microscopy which is used for studying the surface morphology of the materials. Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis as well as chemical characterization of samples. The SEM/ EDX analysis results of flyash are represented in figure-2. The image reveals that most of the particles present in the flyash are irregular in shape and covered with relatively smooth grains of quartz. The EDS data suggest that aluminum, oxygen, carbon, iron, titanium and silicon are the primary elements present in fractions of flyash samples. SEM/EDS provide detailed imaging information about the morphology and surface texture of individual particles as well as elemental composition of flyash samples which also confirms the earlier findings<sup>26</sup>.

**FTIR Analysis:** FTIR spectrum for one of the flyash fraction of size 150  $\mu\text{m}$  is shown in Figure-3. The FTIR data shows the presence of functional groups on the surface of flyash sample. FTIR spectra of flyash sample represent a broad band between 3700cm<sup>-1</sup> - 3100cm<sup>-1</sup> indicating the presence of -OH group on

the sample surface. This stretching vibration is due to the silanol groups (Si-OH) present in the flyash sample. The band observed between  $1250\text{cm}^{-1}$  -  $850\text{cm}^{-1}$  of flyash samples show the presence of  $\text{TO}_4$  (where T = Si, Al) asymmetric stretching vibrations of internal tetrahedral. The bands between  $720\text{cm}^{-1}$ - $650\text{cm}^{-1}$  and  $420\text{cm}^{-1}$ - $500\text{cm}^{-1}$  indicate about the presence of symmetric stretching and  $\text{TO}_4$  bending mode of internal tetrahedral respectively present in flyash samples. In addition, bands appearing between  $800\text{-}600\text{ cm}^{-1}$  are related with tetrahedral vibrations known as secondary building units as well as fragments of aluminosilicate of flyash samples. FTIR studies of this flyash fraction help in the identification of various forms of the minerals present in the sample. The coupled vibrations are found due to the availability of various constituents found in the flyash sample. This result is similar to that reported for a flyash investigated by Dwivedi et.al.<sup>25</sup>.

**Effect of particle size of Adsorbent:** The adsorptive removal of all the four phenols on different particle size (150 to  $45\mu\text{m}$ ) of flyash are studied by variation of contact time (20 to 120 min.) for kinetic modeling and initial phenols concentration (142.85 to 500.00) for equilibrium modeling keeping other parameters constant and the results are shown in Figure 4-5. To reduce the number of figures, only the adsorption of p-chlorophenols having similar shape to other phenols is shown in the Figures. It can be seen from Figures that adsorptive removal of phenols are decreased as follows:  
 $45\mu\text{m} > 100\mu\text{m} > 150\mu\text{m}$ .

This can be explained as amounts of the major constituents of flyash like alumina and silica are increased as the particle size decreased shown in Table-2. The silica and alumina contents of flyash play a significant role in the adsorption of phenols. This is because of the strong chemical bonding between the lone pair of electrons present on the -OH group in the phenol and the central ion of the silicate ( $\text{Si}^{4+}$ ) as well as the presence of a weakly acidic alumina surface<sup>19</sup>. The surface area also increased as the particle size decreased and so active site increased<sup>27</sup>. Hence, in addition to the increase in alumina and silica content with decreasing particle size, the increase in the surface area with availability of more adsorption site also contributed to the observed enhanced adsorptive removal of all four phenols onto the smallest sized fractions of flyash. Among phenols, the removal trend is as follows:  
 $\text{PCP} > \text{MCP} > \text{OCP} > \text{PHL}$

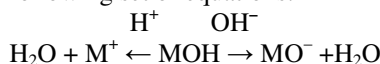
It can be explained as activation of the aromatic ring of monochlorophenols by the chlorine favours the existence of donor-acceptor interactions between the phenolic compounds and the adsorbent surface<sup>28</sup>. It is also obvious that in chlorophenol that both functional groups may be separately or simultaneously involved in the adsorption process. Higher removal of chloro-substituted phenol is due to the introduction of a chloro group (-Cl) into the benzene ring which increase the acidic character (conjugation effect) responsible for forming an anion on the oxygen atom of the -OH group and which has a

strong affinity for alumina and silica surfaces. It is found that adsorption of PCP is higher than that of MCP and OCP. This is because of the position of the -Cl atom in the benzene ring with respect to phenolic -OH substituent strongly influences the adsorption uptake. Aksu and Yener<sup>28</sup> explain this behaviour as a result of steric hindrance between the -Cl and the -OH substituents present in chlorophenols. Similar results are also obtained by Singh et al. in case of phenol<sup>21, 22</sup>.

**Effect of pH:** The effect of pH on phenols removal by flyash is studied by variation of solution pH (2.0 to 10.0) both for kinetic and equilibrium modeling and the results are shown in figure 6-7 and the variations of adsorptive removal values for different pH are as follows:  
 $\text{pH } 2.0 > \text{pH } 4.0 > \text{pH } 6.5 > \text{pH } 8.0 > \text{pH } 10$ .

This can be explained by amphoteric nature of adsorbent and different speciation of phenols molecule with variation of solution pH. The hydrogen ion concentration (pH) primarily affects the degree of ionization of the phenolic adsorbate and the surface properties of the adsorbent. Thus, the pH values of the phenols solution play a significant role in the whole adsorption process. The adsorption is strongly pH- dependent, i.e. it increases with decreasing pH. Any oxide surface creates a charge (positive or negative) on its surface and the magnitude of this charge is proportional to the pH of the solution surrounding the oxide particle<sup>19</sup>.

As mentioned above, the principal constituents of flyash are metal oxides containing mainly Al and Si. Such metal oxides form metal hydroxide complexes at the solution interface leading to the development of a positive or negative charge on the surface. When the pH of the solution decreases, the surface becomes positively charged and the adsorptive removal values towards phenols increases as shown in figure 6-7. Positively charged surface sites on the adsorbent surface favors the adsorption of phenols due to electrostatic attraction. This can be explained on the basis of the formation of a positively charged surface in an acidic medium and a negatively charged oxide surface in a basic medium from the hydroxylated oxide surface of the fly ash. The whole process may be represented by the following set of equations:



At lower pH values, the lone pair of electrons on the oxygen atom of the undissociated -OH group present in the benzene ring coordinated with the highly positively charged surface. A low pH quite probably resulted in lowering the negative charge on the adsorbent surface, thus enhancing adsorption of the negatively charged adsorbate. At higher pH values, the dissociated phenoxide ion ( $\text{C}_6\text{H}_5\text{O}^-$ ) is repelled by the highly negatively charged oxides on the surface. Amongst the phenols studied, this decrease followed the sequence as discussed earlier. Similar observations are observed also by Singh et al. in case of phenol<sup>21, 22</sup>.

**Effect of Initial Concentration:** The uptake of phenol and its chloro-substituted derivatives are studied on flyash at various concentrations (250 to 500 mg/l<sup>-1</sup>) keeping other parameters constant and only one of the plot of para-chlorophenol for kinetic studies are shown in figure-8 because similar plots are obtained for others phenols. It is clear from the figure-8 that adsorption of phenols increased as its concentration increased and finally becomes constant. The initial concentration provides an important driving force to overcome all mass transfer resistance of solutes between the aqueous and solid phases. The higher removal of phenols at initial period may be due to an increased number of vacant sites on the adsorbent available<sup>25</sup>.

This result is consistent with the previously reported results<sup>29</sup>. Thus the adsorptive removal values vary in the order as (500 mg/L) > (350 mg/L) > (250 mg/L)

But among the phenols, the variation is the same as given earlier. Similar observations are observed also by Singh et al. in case of phenol<sup>22</sup>.

**Effect of Temperature:** The effect of temperature for adsorption of phenols on flyash is studied by changing the temperature of the system both for kinetic and equilibrium studies from 30<sup>0</sup>C to 50<sup>0</sup>C and the results are shown in figure 9-10. It is seen from the figures that uptake of phenols increased by increasing temperature indicating endothermic nature of adsorption. This is because of presence of weaker hydrogen bonding (intra and intermolecular) at higher temperature which makes phenols molecule freely available for adsorption<sup>29</sup>. This may be also due to increase in the number of active surface centres available for adsorption as the temperature increased over the range 30-50<sup>0</sup>C. However, the net increase would depend upon the nature of the solute<sup>19</sup>. This suggests that the removal of phenol on flyash involves a chemical process. The increase in uptake of the phenol with temperature may also have been due to a change in the pore size<sup>19</sup>. The variation of the adsorptive removal values at different temperatures with respect to time and concentrations follows the order: 50<sup>0</sup>C>40<sup>0</sup>C>30<sup>0</sup>C.

The variation among phenols examined is the same as discussed earlier. Similar observations are reported by Singh et al. in case of phenol<sup>21, 22</sup>.

**Kinetic Modeling:** The kinetics of adsorption of phenols on flyash is studied on the basis of the most widely used Lagergren equation as shown in equation (1)

$$\log (q_e - q_t) = \log q_e - k t/2.303 \quad (1)$$

Where q (mg g<sup>-1</sup>) is the amount of phenol adsorbed at time t, q<sub>e</sub> (mg g<sup>-1</sup>) is the amount adsorbed at equilibrium and k is equilibrium rate constant of adsorption. The linear plots of log (q<sub>e</sub>-q<sub>t</sub>) vs. t for phenols under different conditions indicate the validity of equation (1) and the process follows first order rate kinetics. Thus, the equilibrium rate constant k values calculated

from one of the linear plots (correlation coefficients ranging from 0.991 to 0.999 indicating about the validity of this equation) corresponding to figure-4,6,8 and 9 according as equation at different conditions are listed in table -4,5,6a,6b and 7. To reduce the number of figures, one of the linear plot of p-chlorophenol at different particle size is shown in Figure-11 because similar plots are obtained for others phenols in different conditions also. Now the kinetic parameters, k for different conditions listed in the table -4, 5,6a and 7 can be summarized as follows,

$$k(45\mu m) > k(100\mu m) > k(150\mu m.)$$

$$k(\text{pH } 2.0) > k(\text{pH } 4.0) > k(\text{pH } 6.5) > k(\text{pH } 8.0) > k(\text{pH } 10)$$

$$k(50^0\text{C}) > k(40^0\text{C}) > k(30^0\text{C})$$

The above trend can be explained as more the adsorption more the rate constant and vice-versa.

However, the sorption rate constant, k, as calculated from linear plot corresponding to Figure-8 according as equation varied in a reverse manner because the fractional adsorption is low at high concentration<sup>19</sup>. Thus, the values of k varied in the order as k (500 mg/L) < k(350 mg/L) < k(250 mg/L). The variation among different phenols is as follows:

$$k(\text{PCP}) > k(\text{MCP}) > k(\text{OCP}) > k(\text{PHL})$$

Similar observations are observed by Singh et al.<sup>22</sup>.

**Equilibrium Modeling:** There are several models available in literature that shows equilibrium relationships between adsorbent and adsorbate. The Freundlich and Langmuir models are the most frequently employed models. In this work, Langmuir model are used to describe the relationship between the amount of phenols adsorbed and its equilibrium concentrations. The linear form of the Langmuir isotherm is given by the relation<sup>21</sup>:

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \quad (2)$$

Where, q<sub>e</sub> is the amount adsorbed at equilibrium (mg g<sup>-1</sup>), Q<sub>0</sub> (mg g<sup>-1</sup>) and b (L mg<sup>-1</sup>) are the Langmuir constants related to the maximum adsorption and energy of adsorption respectively. The plots of C<sub>e</sub> / q<sub>e</sub> vs. C<sub>e</sub> for phenols at different conditions are found to be linear (correlation coefficient ranging from 0.995 to 0.999) indicating the applicability of the Langmuir model. The statistical significance of the correlation coefficient (R<sup>2</sup>) for C<sub>e</sub>/q<sub>e</sub> vs. C<sub>e</sub> is the criteria by which the fitting of the data to Langmuir isotherm is tested. The parameters Q<sub>0</sub> and b have been calculated from the slopes and the intercepts of the linear plots corresponding to the figures-5,7 and 10 according as equation at different conditions shown in Figure-12 and the results are listed in table -4,5 and 6a. To reduce the number of figures, one of the linear plot of p-chlorophenol at different temperature is shown in figure-11 because similar plots are obtained for others phenols in different conditions. The best fit of equilibrium data in the Langmuir isotherm predicted the monolayer coverage of phenol onto flyash. Now the Langmuir Isotherm parameters Q<sub>0</sub> and b for different conditions are listed in the table-4, 5 and 6a can be summarized as follows

$Q_o, b (45 \mu\text{m}) > Q_o, b (106 \mu\text{m}) > Q_o, b (150 \mu\text{m})$   
 $Q_o, b (\text{pH } 2.0) > Q_o, b (\text{pH } 4.0) > Q_o, b (\text{pH } 6.5) > Q_o, b (\text{pH } 8.0) > Q_o, b (\text{pH } 10.0)$   
 $Q_o, b (30^\circ \text{C}) > Q_o, b (40^\circ \text{C}) > Q_o, b (50^\circ \text{C})$

The variation among different phenols is as follows:  
 $Q_o, b (\text{PCP}) > Q_o, b (\text{MCP}) > Q_o, b (\text{OCP}) > Q_o, b (\text{PHL})$

The above trend can be explained as more the adsorption more the isotherm parameters and vice-versa. Similar observations are observed also by Singh et al.<sup>21</sup>.

**Thermodynamic Modeling:** The standard free energy change ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ) and standard entropy change ( $\Delta S^\circ$ ) are calculated using the following equation<sup>19</sup>  
 $\Delta G^\circ = -RT \ln K$  (3)  
 $\Delta H^\circ = RT_1 T_2 / (T_1 - T_2) \ln (K_2 / K_1)$  (4)  
 $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T$  (5)

Where K is equilibrium constant for the adsorption process, which can be expressed as the product of the Langmuir constants  $Q_o$  and  $b$ <sup>30</sup>.

K,  $K_1$  and  $K_2$  are equilibrium constant at temperature T,  $T_1$  and  $T_2$  respectively and R is the gas constant. The thermodynamic parameters are summarized in table- 6b. Positive values of  $\Delta H^\circ$  suggest the endothermic nature of the sorption and the negative values of  $\Delta G^\circ$  indicate the spontaneous nature of the sorption process. However, the values of  $\Delta G^\circ$  decreased with an increase in temperature, indicating that the spontaneous nature of adsorption. The positive value of  $\Delta S^\circ$  shows the increased randomness of the solid/solution interface during the adsorption of phenols on flyash. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational

energy than the energy lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. The positive value of  $\Delta S^\circ$  also shows affinity of adsorbent for phenols. The enhancement of adsorption at higher temperatures may be attributed to the enlargement of pore size or activation of the adsorbent surface<sup>31</sup>. Similar observations are observed also by Singh et al.<sup>21</sup>.

**Table -1**  
**Characteristics of flyash**

Element as oxide	Weight %
SiO <sub>2</sub>	59.54
Al <sub>2</sub> O <sub>3</sub>	27.20
Fe <sub>2</sub> O <sub>3</sub>	4.87
CaO	2.91
MgO	0.40
K <sub>2</sub> O+Na <sub>2</sub> O	1.00
LOI ( 800 <sup>0</sup> C)	12.00
Specific gravity	1.80
Surface Area	7000 – 9000 cm <sup>2</sup>
Porosity	0.34 - 0.62

**Table-2**  
**Chemical analysis for fractions of flyash Chemical Composition (Percentage by weight)**

Particle Size $\mu\text{m}$	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	LOI 800 <sup>0</sup> C
150 $\mu\text{m}$	59.54	27.20	4.87	2.91	0.40	12
106 $\mu\text{m}$	67.00	30.00	6.10	3.80	1.10	08
45 $\mu\text{m}$	77.75	36.00	6.00	4.00	1.50	4.09

**Table-3**  
**XRF analysis for fractions of flyash**

Chemical composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	SrO	SO <sub>3</sub>
Weight(%) 150 $\mu\text{m}$	59.817	24.290	6.664	1.599	0.254	0.120	2.082	4.314	0.044	0.001	0.056	0.001
Weight(%) 106 $\mu\text{m}$	60.250	24.373	6.576	1.513	0.248	0.077	1.841	1.841	0.042	0.001	0.054	0.001
Weight(%) 45 $\mu\text{m}$	60.420	25.339	6.192	1.473	0.306	0.071	1.711	3.505	0.040	0.017	0.052	0.012

**Table-4**  
**Adsorption Kinetic and Isotherm parameter for different fractions of flyash**

Adsorbate	Particle Size of Adsorbent ( $\mu\text{m}$ )	Rate Constant		Langmuir Parameters		
		$k (\text{min}^{-1}) \times 10^{-2}$	$R^2$	$Q_0 (\text{mmol g}^{-1}) \times 10^{-2}$	$b (\text{L mol}^{-1}) \times 10^3$	$R^2$
Phenol	150	3.68	0.991	3.73	1.90	0.998
	106	3.92	0.991	3.97	2.12	0.999
	45	5.53	0.993	5.01	2.17	0.998
o-chlorophenol	150	4.14	0.977	7.18	2.71	0.995
	106	4.38	0.982	7.56	3.93	0.999
	45	4.83	0.989	8.24	4.20	0.999
m-chlorophenol	150	4.83	0.994	8.93	2.93	0.999
	106	5.07	0.990	9.67	4.80	0.999
	45	5.56	0.993	10.20	7.42	0.999
p-chlorophenol	150	5.07	0.994	10.45	3.49	0.998
	106	5.36	0.995	10.90	5.41	0.999
	45	5.76	0.986	11.69	7.92	0.998

Adsorption Kinetic condition: pH 6.5 and Temperature 30°C. Isotherm conditions: pH 6.5; Temperature 30°C and concentration 500  $\text{mgL}^{-1}$

**Table-5**  
**Adsorption Kinetic and Isotherm parameter for different pH values of flyash**

Adsorbate	pH	Rate Constant		Langmuir Parameters		
		$K (\text{min}^{-1}) \times 10^{-2}$	$R^2$	$Q_0 (\text{mmol g}^{-1}) \times 10^{-2}$	$b (\text{L mol}^{-1}) \times 10^3$	$R^2$
Phenol	2.0	4.38	0.987	4.43	2.16	0.998
	4.0	3.92	0.989	4.07	2.09	0.998
	6.5	3.68	0.997	3.73	1.90	0.998
	8.0	3.22	0.992	3.34	1.80	0.995
	10.0	2.99	0.988	2.90	1.42	0.998
o-chlorophenol	2.0	4.84	0.978	4.74	3.92	0.999
	4.0	4.61	0.978	4.63	2.87	0.997
	6.5	4.15	0.994	4.35	2.71	0.995
	8.0	3.92	0.979	4.16	2.15	0.989
	10.0	3.46	0.977	3.78	1.98	0.989
m-chlorophenol	2.0	5.76	0.992	5.98	6.35	0.998
	4.0	5.29	0.993	5.64	4.55	0.999
	6.5	4.84	0.994	5.40	2.93	0.999
	8.0	4.38	0.993	5.11	2.23	0.999
	10.0	3.92	0.986	4.92	1.78	0.996
p-chlorophenol	2.0	5.99	0.987	6.65	8.81	0.997
	4.0	5.29	0.994	6.13	5.46	0.999
	6.5	5.06	0.994	6.32	3.45	0.998
	8.0	4.84	0.998	6.27	2.56	0.995
	10.0	4.15	0.999	5.98	2.17	0.990

Kinetic conditions size 150 $\mu\text{m}$ ; Temperature 30°C and concentration 500  $\text{mgL}^{-1}$  Isotherm condition: size 150 $\mu\text{m}$  and Temperature 30°C.

**Table-6a**  
**Adsorption Kinetic and Isotherm parameter for different temperatures**

Adsorbate	Temperature (°C)	Rate Constant		Langmuir Parameters		
		K (min <sup>-1</sup> ) x 10 <sup>-2</sup>	R <sup>2</sup>	Q <sub>o</sub> (mmol g <sup>-1</sup> ) x 10 <sup>-2</sup>	b (L mol <sup>-1</sup> ) x 10 <sup>3</sup>	R <sup>2</sup>
Phenol	30±1	3.68	0.991	3.73	1.90	0.998
	40±1	3.92	0.999	4.27	2.03	0.999
	50±1	4.15	0.999	4.70	2.45	0.999
o-chlorophenol	30±1	4.15	0.977	4.35	2.73	0.995
	40±1	4.38	0.972	4.50	3.69	0.999
	50±1	4.60	0.946	4.77	4.86	0.999
m-chlorophenol	30±1	4.84	0.994	5.40	2.93	0.999
	40±1	5.07	0.994	5.81	4.68	0.999
	50±1	5.30	0.992	6.12	6.94	0.997
p-chlorophenol	30±1	5.07	0.994	6.32	3.50	0.998
	40±1	5.30	0.999	6.48	7.06	0.999
	50±1	5.76	0.999	6.95	11.06	0.998

Kinetic conditions: pH6.5; size 150µm and concentration 500 mgL<sup>-1</sup> Isotherm condition: pH 6.5 and size 150µm.

**Table-6b**  
**Thermodynamic Parameters at different temperatures**

Adsorbate	Temperature (°C)	K	Langmuir Parameters		
			ΔG° (k cal mol <sup>-1</sup> )	ΔS° (cal mol <sup>-1</sup> )	ΔH° (k cal mol <sup>-1</sup> )
Phenol	30	70.87	- 2.5563	20.9168	3.7815
	40	86.68	-2.7654	26.9957	5.6852
	50	115.15	-3.0354	-	-
o-chlorophenol	30	118.76	-2.8660	30.2314	6.2941
	40	166.05	-3.1683	31.4620	6.6793
	50	231.82	-3.4829	-	-
m-chlorophenol	30	158.22	-3.0381	43.5848	10.1681
	40	271.91	-3.4739	39.6211	8.9275
	50	424.73	-3.8701	-	-
p-chlorophenol	30	221.20	-3.2391	55.7257	13.6458
	40	457.49	-3.7964	45.3153	10.3873
	50	768.67	-4.2495	-	-

Conditions: pH 6.5 and Size 150µm.

**Table-7**  
**Adsorption Kinetic Parameter at different concentrations**

Adsorbate	Concentration mgL <sup>-1</sup>	Rate constant k (min <sup>-1</sup> ) x 10 <sup>-2</sup>	R <sup>2</sup>
Phenol	500	3.68	0.991
	350	4.15	0.999
	250	4.38	0.997
o-chlorophenol	500	4.15	0.977
	350	4.38	0.967
	250	4.60	0.956
m-chlorophenol	500	4.84	0.994
	350	5.06	0.993
	250	5.53	0.991
p-chlorophenol	500	5.07	0.994
	350	5.53	0.988
	250	5.76	0.992

Conditions: pH 6.5, Size 150µm and temperature 30°C.

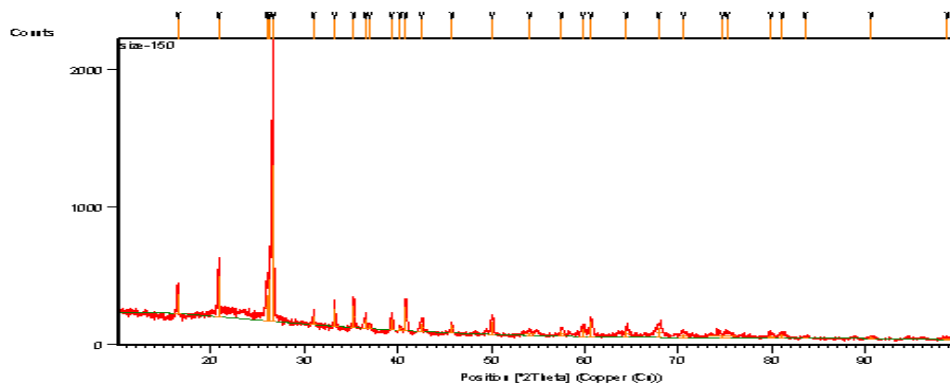


Figure-1  
X-ray diffractogram of flyash (150 μm)

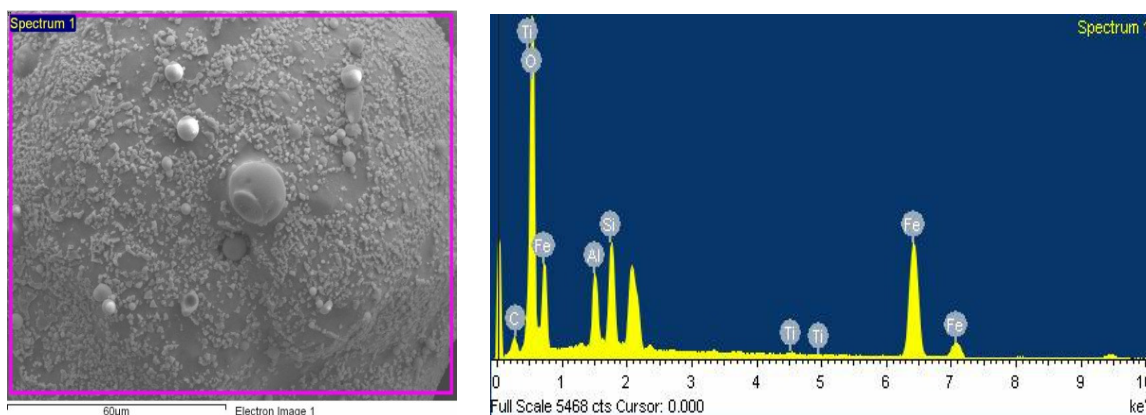


Figure-2  
SEM-EDX photograph of flyash(150 μm)

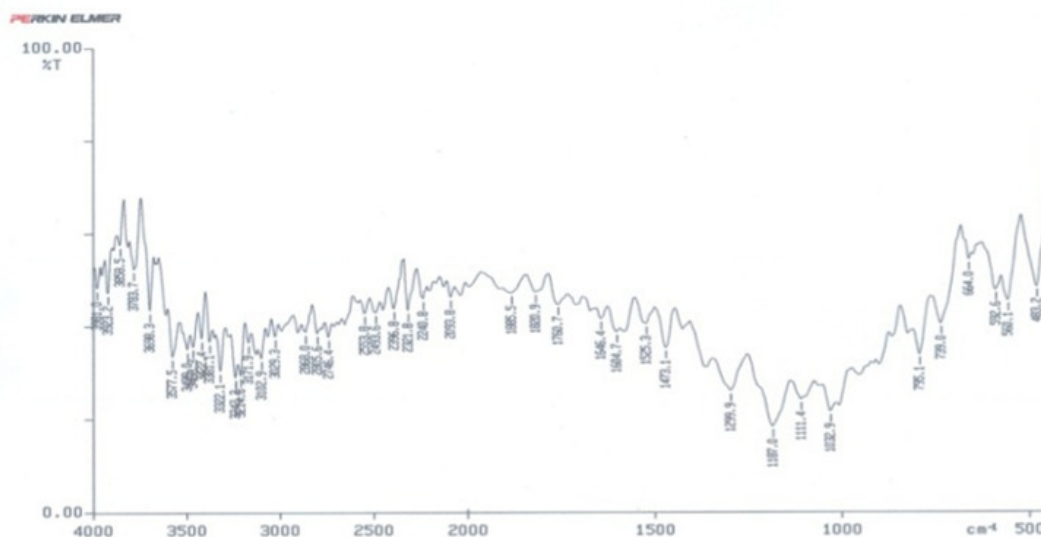
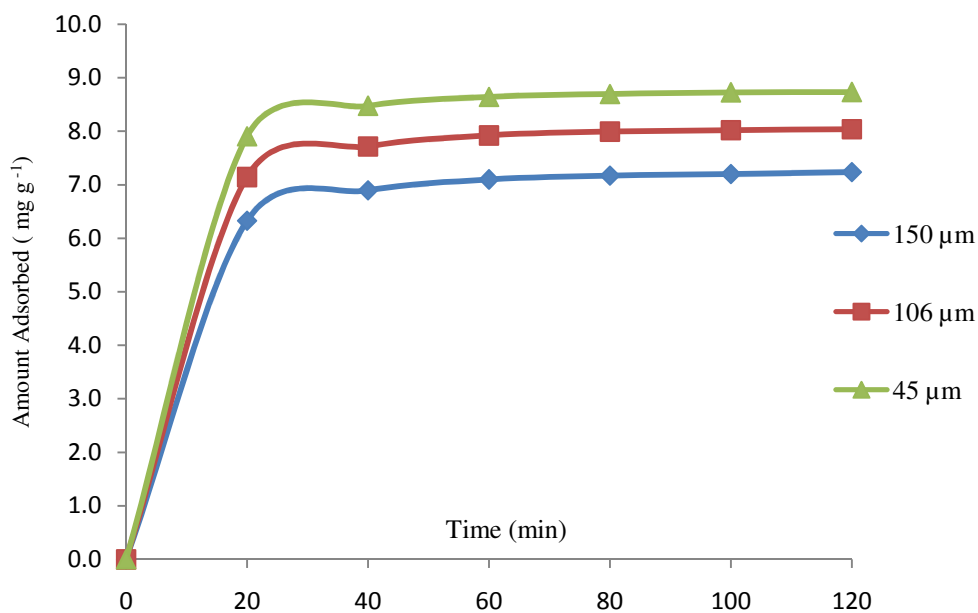
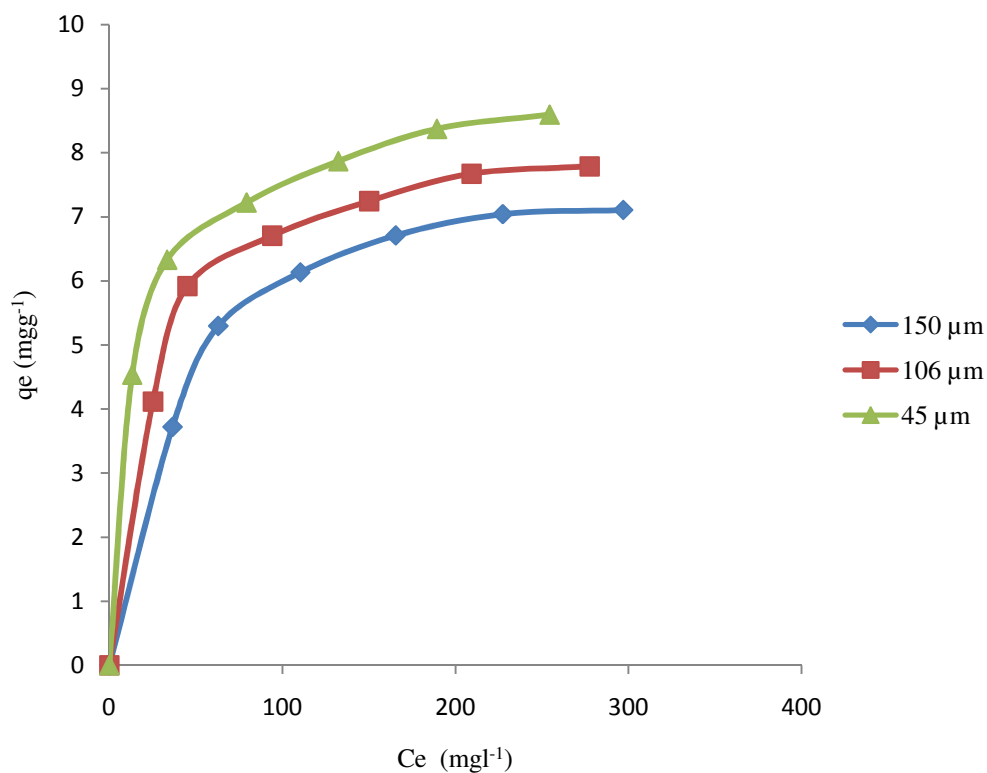


Figure-3  
FTIR spectrum of flyash (150 μm)





**Figure-4**  
Adsorption Kinetics of p - chloro phenol on flyash; condition: 500 mg l<sup>-1</sup>; pH 6.5; Temperature 30°C



**Figure-5**  
Adsorption Isotherm for p - chloro phenol on flyash. Condition: Different Size; Temperature 30°C; pH 6.5

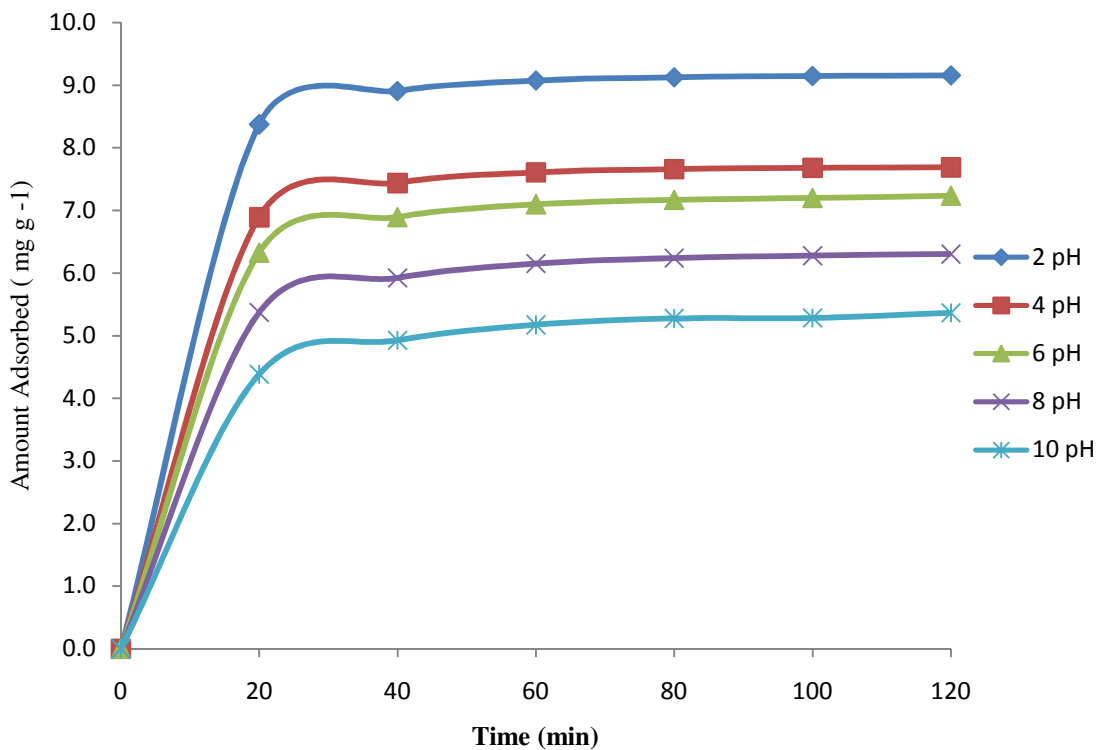


Figure-6  
 Adsorption Kinetics of p - chloro phenol on flyash; condition: 500 mg l<sup>-1</sup>; size 150 μm; Temperature 30°C

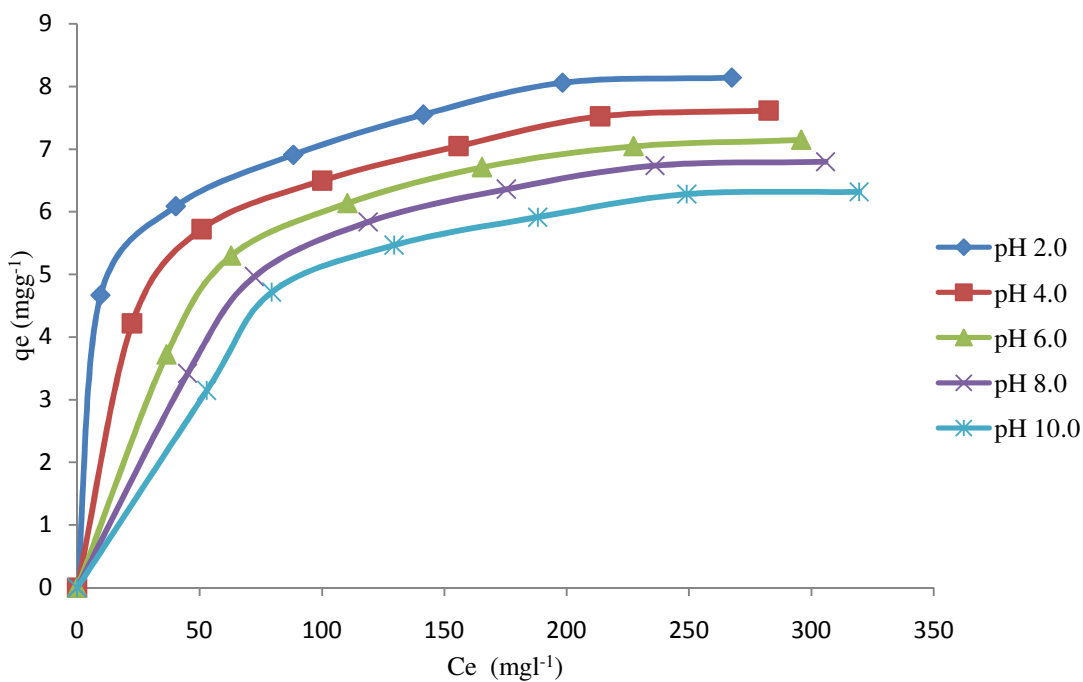
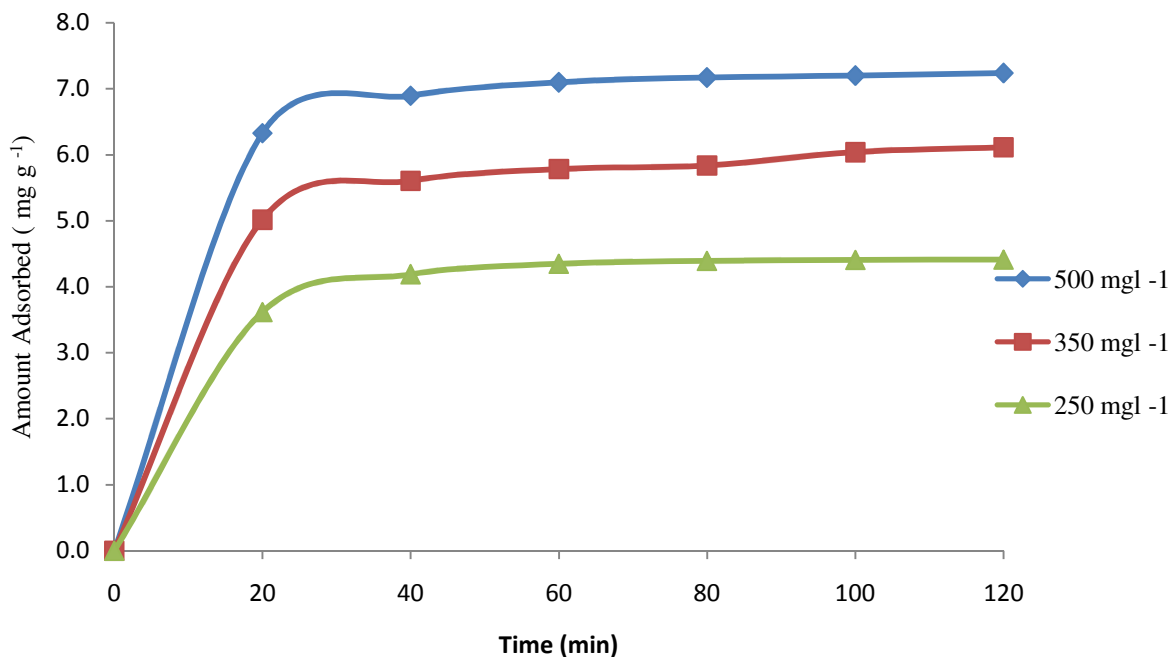
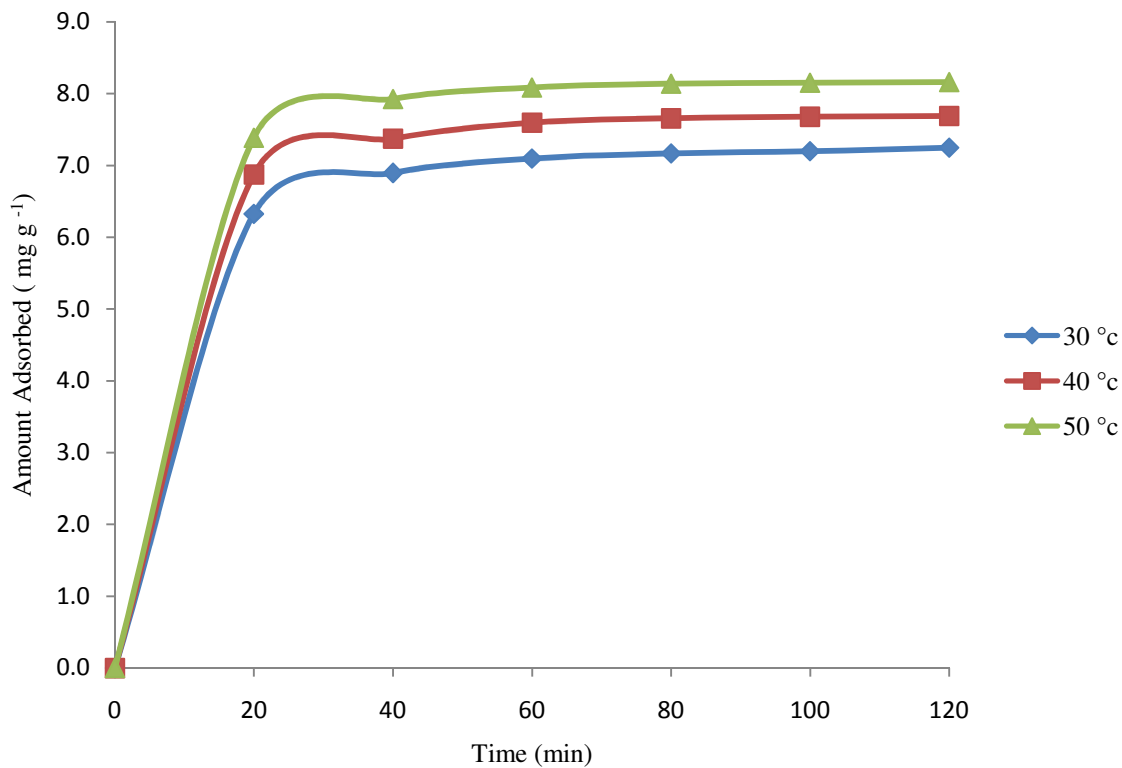


Figure-7  
 Adsorption Isotherm for p - chloro phenol on flyash condition: Different pH; Particle size 150 μm; Temperature 30°C



**Figure-8**  
Adsorption Kinetics of p - chloro phenol on flyash; condition: pH 6.5; size 150  $\mu$ m; Temperature 30°C



**Figure-9**  
Adsorption Kinetics of p - chloro phenol on flyash; condition: 500 mg l<sup>-1</sup>; pH 6.5; size 150  $\mu$ m

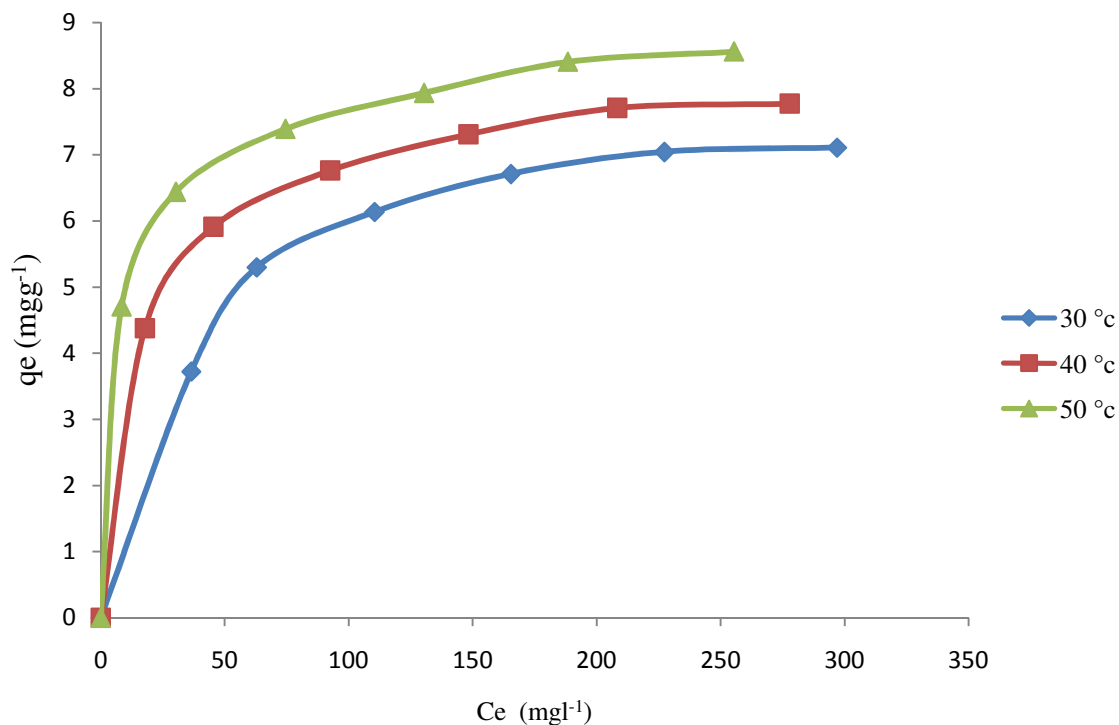


Figure-10

Adsorption Isotherm for p-chloro phenol on flyash, Condition: Different Temperature; Particle size 150 μm; pH 6.5

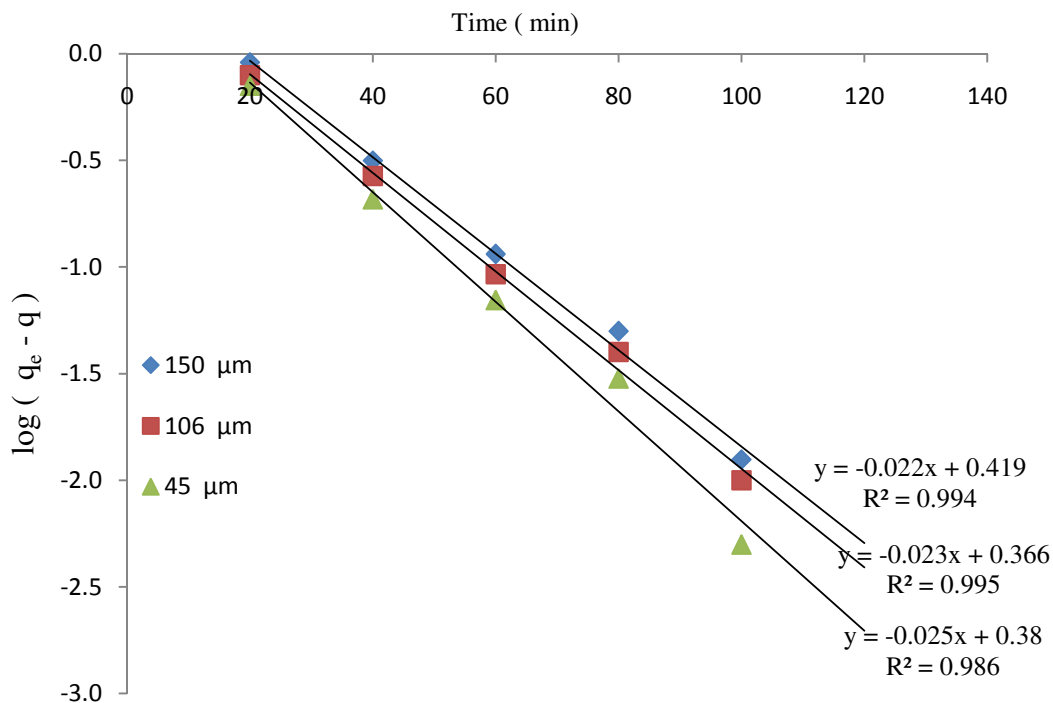


Figure-11

Lagergren plot for the adsorption of p-chlorophenol on flyash; Concentration 500 mg/l; pH 6.5; Temperature 30°C

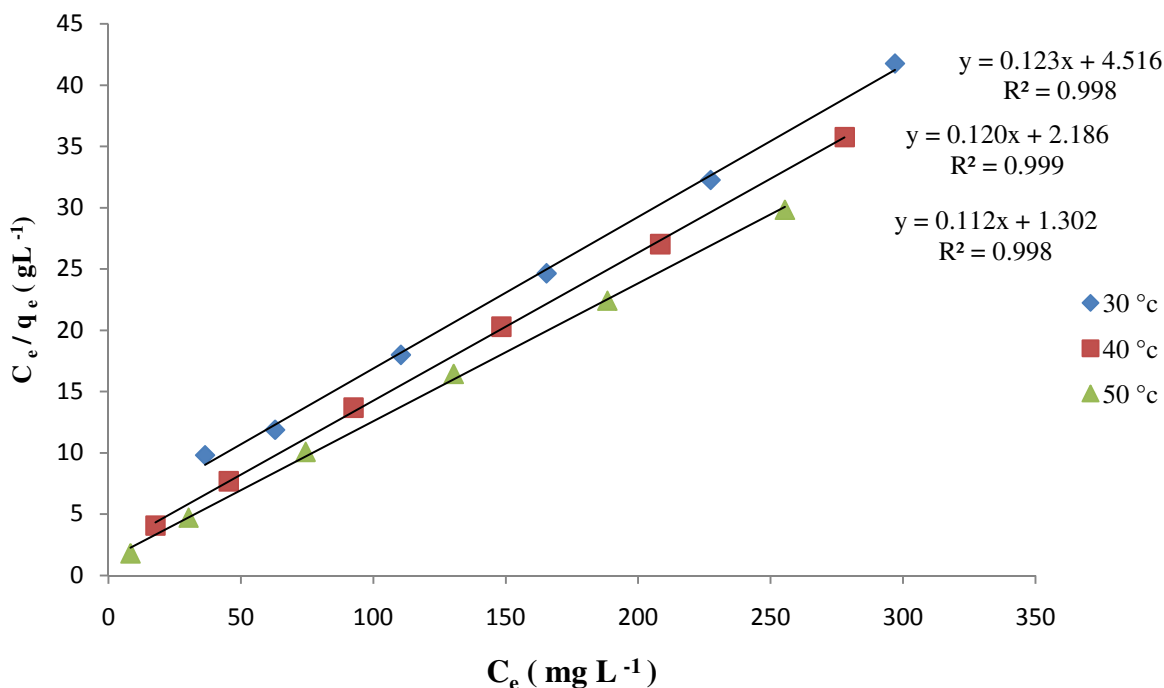


Figure-12  
Langmuir plot for the adsorption of p - chlorophenol on flyash. Particle size 150  $\mu\text{m}$ ; pH 6.5

## Conclusion

The present study reports characteristics of adsorbent through a number of experimental approach as well as batch type kinetic and equilibrium adsorption showing the potentiality of flyash for phenolic wastewater treatment. This treatment is simple and economic. Equilibrium data fitted very well to Langmuir model confirming monolayer coverage of phenol onto flyash. It can be concluded that some industrial waste by-products as alternative adsorbents for the adsorption of organics like phenols from aqueous solution can be used due to easily available, low cost and easy handling. Decreasing particle size and pH and increasing temperature increases the adsorption parameters of flyash for phenols. The kinetic and equilibrium data thus generated can be used for designing a treatment plant for phenolic effluents wherein continuous removal or recovery can be achieved on a large scale.

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