Study on Adsorption for Removal of Commercial Phenyl by Fly Ash

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ABSTRACT

The aim of this present work is to investigate the sorption potential of a modified and unmodified fly ash as a law-cost adsorbent material for the removal of phenyl from aqueous medium. In this regard fly ash is a very attractive option, because it is cheap, widely available and has good mechanical stability for handing purposes and employment in adsorption columns. The effect of various factors such as contact time, adsorbent dosage, amount of initial adsorbent. A concentration on the sorption process was investigated under batch equilibrium technique using UV/Vis Spectrometry. The result obtained showed that the capacity of fly ash for adsorption of Phenyl depends on the initial PH and concentration of solutions.

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Introduction

The use of organic compounds as a phenyl in industry such as dyestuffs, Pharmaceuticals, pesticides, agriculture, tanning etc. is of growing concern for environmentalists, due to toxic effect of these compounds to aquatic and human beings. However, these toxicants enter aqueous stream through discharges from these industries and municipal wastes (walter andLuthy,1984[1] Mckay et.al., 1985[2]). Waste water containing phenolic compounds are a serious environmental problem, and this water cannot simply be released into the environment without treatment. The toxic and hazardous nature of phenols and their derivatives have been well documented (Greminger et al.,1982[3], Brandt et al., 1997[4], Bulbul et al., 1997[5], Denizli et.al., 2004[6]) and can cause several health problems (Slein and Sansone, 1980[7]). Phenolic compounds have been classified as high-priority pollutants by the USA EPA (Environment Protection Agency, 1984[8]). Phenolic compounds are usually present in wastewater generated from the paint, solvent, petrochemical, coal conversion, pharmaceutical, plastic, iron-steel and paper and pulp industries. The presence of phenyl and derivatives in waste water are of much concern because of their toxicity and threat to human life environment. The origin is both anthropogenic and xenobiotic. Xenobiotic sources are industrial wastes derived from fossil fuel extraction, chemical process industries such as phenol manufacturing plants, pharmaceutical industries, wood processing industry and pesticide manufacturing plants (Fawzi et al.,2000[9] Nagda et al.,2007[10]). Anthropogenic sources are from forest fire, natural runoffs from urban area where asphalt is used as binding material and natural decay of lignocellulose materials Kumaran(1986[11]). Phenol and its derivatives are considered noxious pollutants because they are toxic and harmful to living organisms at low concentrations. The utilization of phenol contaminated waters causes protein degeneration, vomiting, smoky *coloured* urine, paralysis of the central nervous system and also damages the kidney, liver and pancreas in human body Kumar and Min (2011[12]). Phenol at concentration as low as 5.0×10^3 mg/l imparts a typical smell upon chlorination and that is why WHO (1984) has prescribed a concentration of 1.0×10^3 mg/l as the guideline concentration for drinking water. Elimination of phenolic compounds thus is a necessity to preserve the environmental quality. In view of these discharge of toxic compounds into stream, rivers and lakes, the water needs to be purified by several techniques but the adsorption technique is widely used due to its high rate, high uptake capacity, low cost and regeneration (Saleem et.al., 1993[13]) The adsorption of organic compound on the surface of fly ash has been studied extensively by other workers (Uranowski 1998[14],Tanju and Janes 1999[15], lin and Liu 2000[16],Yu and Chou 2000[17]). The adsorption of phenyl and its analogues from contaminated water onto fly ash has been investigated (Sakar and Acharya, 2006[18]). The Potential of fly ash as a substitute for activated fly ash has been examined (Aksu and Yener, 1999[19]).

. Fly ash is particulate material produced from the combustion of coal. The removal of heavy metals from effluents and wastewaters by adsorption on fly ash has been studies by a number of researchers. Fly ash is strong alkali materials, which exhibits pH of 10-13 when added to water, and its surface is negatively charged at high pH, In view of this, it can be expected that metal ions or organic materials can be removed from aqueous solutions by precipitation or electrostatic adsorption. Bayat (2002[20],a and b), studied the effectiveness of removal of Ni, Cu, Zn, Cr and Cd by fly ash. Alinnor (2007[21]) worked on the removal of Pb^{2+} and Cu^{2+} from aqueous solution using fly ash as adsorbent. Mavros et al (1993[22]) used two different types of fly ash (from the coal fields of Kardia and Megalopolis in Greece) to remove Ni from wastewater. Weng and Huang (1994[23]) investigated that fly ash can be used as an effective adsorbent for Zn and Cd to clean up dilute industries wastewater. Heechom et al (2005[24])

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reported removal characteristics of heavy metals from aqueous solution by fly ash. Removal of toxic solvents from polluted environment can be achieved by several techniques but the adsorption technique is widely used due to its high rate, high uptake capacity, effective treatment in dilute solution, low cost and regeneration. Adsorption is a reliable technique that achieves rapid results. Adsorption of organic compound on the surface of fly ash has been studies extensively. A lot of studies were conducted to show the effectiveness of fly ash in the removal of organic materials from aqueous solution. The adsorption of phenol and its analogous from contaminated water onto fly ash has been investigated by Sarkar and Acharya (2006[18]). The potential of fly ash as a substitute for activated fly ash was examined by Aksu and Yener (1999[19]). The result obtained showed that the capacity of fly ash for absorption of phenyl depends on the initial pH and phenyl concentration. Kumari et al. (1988[25]) has reported the use of fly ash for the removal of phenyl. The most important characteristics of fly ash are calcium content that provides alkalinity in the system raising pH to strongly alkaline valves (~12) and the($SiO_2+Al_2O_3+Fe_2O_3$) content. The effect of surface modification of fly ash on the adsorption of organic compounds has been studied by earlier researches (kaneko et al 1988[26], Asakwa et al 1985[27], zawadzki 1988[28]) and it has been observed that surface modification has a pronounced effect on adsorption. But work on the removal characteristics of phenyl from aqueous solution by fly ash modified with citric acid is very scanty.

Methods and Methodology

0.5g portions of Fly ash were taken in different Erlenmeyer Flasks. 100 $cm^3$of phenyl solutions was added to each flask having different concentrations. The flask containing Fly ash and phenyl was agitated in water bath for different duration of time at 30^0C using magnetic stirrer. The slurry formedwas then filtered through ordinary filter paper. The clear filtrate was thenanalyzed for phenyl content is Spectrophotometer at wavelength 240 nm.Blank determination was performed under similar experimental conditions.The amount of phenyl adsorbed by the Fly ash at equilibrium was calculated using the following expression Han et.al., (2006[29])

$q_e = v(C_0-C_e)/1000m$ (1)

Where

q_e = the amount of phenol adsorbed at equilibrium (mg/kg),

V = the sample volume (ml),

C_0 = the initial phenyl conc.

C_e = the equilibrium phenyl conc.

m = the dry weight of the fly ash.

The reported valves of phenyl adsorbed by fly ash in each test were the average of at least three measurements (Alinnor and Ejike, 2007[30]). At the end of agitation period, the phenyl adsorbed by Fly ash was determined as described above. The concentration changes of the individual compounds in the solutions were determined by means of UV-VIS Spectrophotometer (SQ-4802 Double Beam).

The maximum absorbance's for each solute from the highest standard solution prepared were found using scanning spectrophotometer at the respective wave length maxima λmax . The λmax used were 240 nm for phenyl.

The Calibration curve plot of absorbance v/s concentration for the entirestandard showed a linear working range. The supernatant solution obtained after adsorption were also analyzed using the same wavelengths.

The correlation coefficient value determined for each of the adsorption isotherm indicates that the Freundlich model effectively fits the experimental data.

Table 1 . Concentration V/S Absorption.

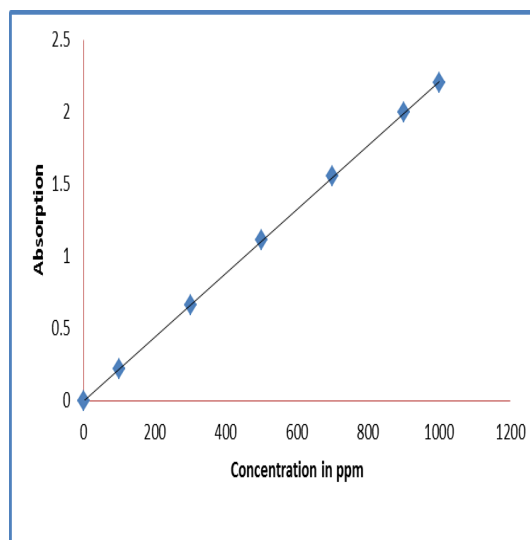| S. NO.	Concentration in ppm	Absorption
1	0	0.000
2	100	0.217
3	300	0.663
4	500	1.114
5	700	1.558
6	900	1.993
7	1000	2.199

Fig 1. Calibration curve.

Composition of Fly Ash

In the investigation of fly ash following compounds are present in fly ash with in weight in percentage.

Table 2. Chemical composition of fly ash determined by XRF technique.

Chemical composition (%)	(%) Value
SiO_2	63.24
Al_2O_3	22.63
Fe_2O_3	4.76
CaO	3.60
K_2O	3.15
MgO	1.69
SO_3	1.68
TiO_2	1.29

Other Compounds-
Cl(0.50%), Na_2O(0.30%), P_2O_5(0.24%), WO_3(0.11%), ZrO_2(0.04%), MnO
(0.04%), Cr_2O_3(0.02%), SrO(0.02%), CoO(0.02%), ZnO(0.02%), NiO(0.01%),CuO(97PPM), Rb_2O(86PPM), Br(51PPM), Y_2O_3(49PPM), SeO_2(44PPM),Nb_2O_5(40PPM).

Properties of Fly Ash
Physical

Fly ash consists of fine, powdery particles that are predominantly spherical in shape, either solid or hollow, and mostly glassy (amorphous) in nature. The carbonaceous material in fly ash is composed of angular particles. The particle size distribution of most bituminous coal fly ashes is generally similar to that of silt (less than a 0.075 mm or No. 200 sieve). Although sub bituminous coal fly ashes are also silt-sized, they are generally slightly coarser than bituminous coal fly ashes. The particle size distribution of raw fly ash is

very often fluctuating constantly, due to changing performance of the coal mills and the boiler performance. The specific gravity of fly ash usually ranges from 2.1 to 3.0, while its specific surface area (measured by the Blaine air permeability method) may range from 170 to 1000 mg/kg.

The color of fly ash can vary from tan to gray to black, depending on the amount of unburned carbon in the ash. The lighter the color, the lower the carbon content. Lignite or sub bituminous fly ashes are usually light tan to buff in color, indicating relatively low amounts of carbon as well as the presence of some lime or calcium. Bituminous fly ashes are usually some shade of gray, with the lighter shades of gray generally indicating a higher quality of ash. The nature and composition of fly ash are influenced by the coal origin and the existing burning condition under which it were formed. Therefore, it is to be expected that these ashes should have different adsorption capacities for the uptake of adsorbents. The adsorption capacity for the fly ash used by Sarkar et al.,(2005[31]) was found to be higher than the fly ash used in this investigation. Furthermore, the result was also in contrast with the finding of Ahmaruzzaman and Sharma(2005[32]) and this is due to the fact that the fly ash used in their investigation had a higher specific surface area .

Chemical

The chemical properties of fly ash are influenced to a great extent by those of the coal burned and the techniques used for handling and storage. There are basically four types, or ranks, of coal, each of which varies in terms of its heating value, its chemical composition, ash content, and geological origin. The four types, or ranks, of coal are anthracite, bituminous, sub bituminous, and lignite. In addition to being handled in a dry, conditioned, or wet form, fly ash is also sometimes classified according to the type of coal from which the ash was derived. The principal components of bituminous coal fly ash are silica, alumina, iron oxide, and calcium, with varying amounts of carbon, as measured by the loss on ignition (LOI). The LOI for fly ash should be less than 6 %. Lignite and sub bituminous coal fly ashes are characterized by higher concentrations of calcium and magnesium oxide and reduced percentages of silica and iron oxide, as well as lower carbon content, compared with bituminous coal fly ash. Very little anthracite coal is burned in utility boilers, so there are only small amounts of anthracite coal fly ash.They consist mostly of silicon dioxide (SiO_2), which is present in two forms amorphous, which is rounded and smooth, and crystalline, which is sharp,pointed and hazardous; aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3).

Freundlich Isotherm

The Freundlich isotherm were development using the linearized Freundlich equation. The Freundlich adsorption isotherm can be written in the form.

$$\text{Log } q_e = \log K + 1/n \log C_f \qquad (2)$$

Where:-

q_e = The mass of contaminant adsorbed per unit mass.

K= adsorption Capacity, Freundlich Constant

n = strength of adsorption, freundlich constant

C_f = Final Concentration of Contaminant

The term q_e was determined by taking the difference in the initial and final concentration of the target contaminant in each isotherm run and dividing it by the mass of fly ash added to the system. All target concentration change was attributed to

adsorption to the fly ash. The log q_e was graphed verses log C_f to develop the Freundlich isotherm plot. A linear trend line was added to the plot using Microsoft excel from which the slope and Y intercept were determined. The Slope represents the Valve for 1/n and y-intercept represent the valve taken as k. The Freundlich isotherm predicts that adsorbate concentration on the surface of an adsorbent will increase when there is an increase in the initial adsorbate concentration in the aqueous solution. The experimental data obtained are plotted as log Qe verse log C_f, to obtain the constants Kf and

1/n. The constant K_f is a comparative measure of the adsorption capacity of the adsorbent, while n is an empirical constant. The magnitude of n given an indication of the favorability of adsorbent/adsorbate system. Value of n>1 signify that the solute has a low affinity for the adsorbent at low concentration.

Results and Discussion

The results are reported in term of removal of phenyl. Effects of initialphenyl concentration, amount of fly ash, contact time have been investigated for phenyl removal. Concentrations of adsorbed and unabsorbed phenyl are estimated for each experimental solution.

1. Effect of Initial Phenyl Concentration

The influence if initial concentration on the removal of phenyl by fly ash samples was studied at initial concentration of 100-200mg/l and the result presented in fig.2
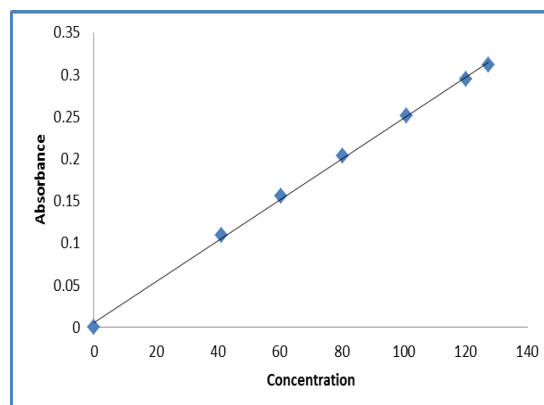

Fig 2. Effect of initial concentration on the adsorption of phenyl from solution.

Fig 2 shows that sorption capacity of phenyl on adsorption increase with increase in phenyl concentration. The increase in adsorption capacity with increasing in adsorption capacity with increasing phenyl compound concentration phenyl compound concentration could due to higher probability of collision between phenyl compound and adsorbent surface. Noeline et.al. (2005[33]) solubility and the nature of adsorbent play a significant role in adsorption . A decrease in solubility in solubility and Pka is associated with an increase in adsorption capacity. This agrees with the observation of Hamdaoui and Naffrechoux, (2007[34]) that attributed higher phenyl molecular weight and cross sectional area.

2. Effect of Contact Time

In order to find out the time for equilibrium adsorption, the interaction period for phenyl on the powdered fly ash was varied and the percent adsorption was plotted for different time interval. It was found that at the initial stage, rate of

adsorption of phenyl is quite high and reaches a maximum after 10 min. that does not charge with further elapse if time fig.3
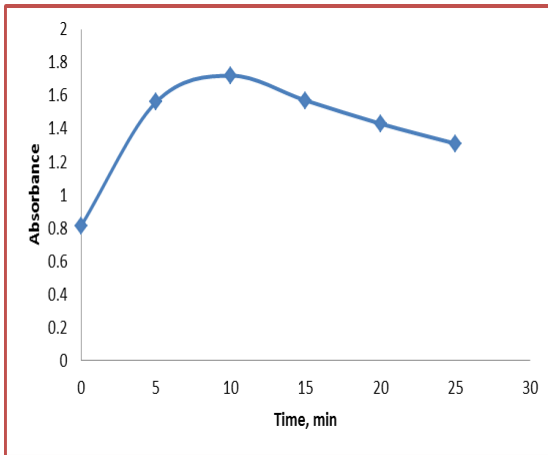

Fig 3. Effect of contact time on the percentage removal of Phenyl from solution.

The saturation curves rises sharply in the initial stage, including that there are plenty of readily accessible sites. Eventually a plateau, is reached in all curve indicating that adsorbent is saturated at this level (Vadivelan andKumar, 2005[35] ,uddin et.al. 2007[36], Nagda et.al.,2000[37]) the percentage removal of phenyl at this equilibrium time (10 min.) is found. It is a proven fact that adsorption equilibrium time dependent on the type of adsorbent. Kannam and Krauppasmy (1998[38]) using fly ash powdered and saw dust obtained adsorption equilibrium contact time Singh et.al.,(1994[39]) reported that for impregnated fly ash, the maximum removal of phenyl was found at contact time of Qadeer and Rehan (2002[40]) worked on a fly ash and observed that the adsorption of phenyl was instant attaching equilibrium within 5 minutes.

3 Variation with amount of adsorbate

The determination of optimum dose is essential for optimization of removal process. It is observed that with a slight increase of dose of the fly ash for an initial phenyl solution. Concentration the adsorption decrease. this can be attributed to decrease adsorbent surface area and availability of less adsorption sited resulting from the decrease adsorbent dosage as observed by Srivastava et.al.,(2006[41]),It can be concluded that the rate of phenyl compound binding with adsorbents decrease more rapidly in the initial stages.
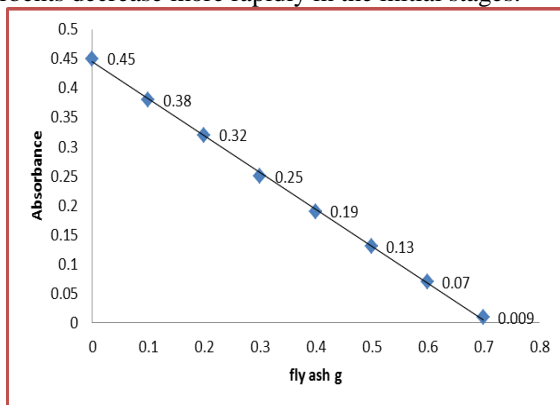

Fig 4. Effect of fly ash the percentage removal of Phenyl from Solution.

Adsorption Isotherm

Sorption equilibrium provides fundamental physiochemical data for evaluating the applicability of sorption process as a unit operation. In the present investigation the equilibrium data were analysed using Freundlich isotherm method. To facilitate the estimation of the sorption capacities, experimental data from the initial concentration were fitted to Freundlich equilibrium adsorption isotherm. In order to facilitate the estimation of the adsorption capacities at various conditions.

The experimental equilibrium data was also analysed using the Freundlich isotherm models. The Freundlich isotherm was adapted to characterize the adsorption intensity of phenyl by fitting the experimental data. The linearised form of the Freundlich equation is

Log qe=Log Kf+ 1/n log Ce (3.1)

Where qe is the adsorption capacity (mg/g), Ce is the concentration of the adsorbent in solution at equilibrium (mg/dm3), Kf and n are the Freundlich constants. If a plot of log qe against log Ce yields a straight line, then the sorption process obeys a Freundlich adsorption. The Kf and 1/n can be Obtained from the intercept and slope of the straight line. The linearized Freundlich adsorption isotherm of phenyl on a fly ash are shown here.
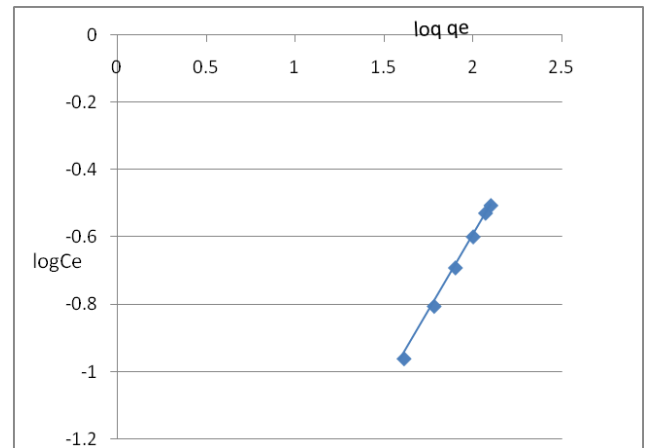

Fig 5 Freundlich adsorption isotherm of phenyl on a fly ash

The coefficient of determination (R^2) valves given the explanatory power of the model. The closer the R^2 valves are to unity, the more the estimated model is believed capable of governing the data set. The lower R^2 valves obtained for phenyl on the Freundlich isotherm. Similar observation were reported by (Aktas and Cecen, 2007[42] , Mahvi et al.,2004[43] and dursun and Kalayei 2005[44]).The higher valve of Kf the Freundlich constant, showed easy uptake of phenyl from aqueous solution (Rengaray et al., 2002[45])

Table 3. Valve of Freundlich constant for adsorption of Phenyl on fly ash.

Adsorbents/Adsorbate	Freundlich constants		
	Adsorption capacity kf (mg/g)	intensity absorption n(l/mg)	R^2
Fly ash	0.002	0.003	1
	0.002	0.003	1
	0.002	0.005	0.99
	0.002	0.005	0.99
	0.002	0.006	0.99

The intensity of adsorption (n) was higher for phenyl. The trend of result showed that phenyl because of its higher adsorption on fly ash would be preferentially sorbed then phenyl. the intensity of adsorption valves obtained for phenyl

on fly ash are higher than the results of sarkar et.al.,(2006[45]) for phenyl on fly ash and Mahvi et.al.,(2004[43]) on rice husk.

Table 4. XRD Details of fly ash.

| POS [^{0} 2 Th]	FWHM [^{0} 2 Th]	D SPACING [A^0]	Rel. int. [%]	Area [cts x ^{0} 2 Th]	Particles size [nm]
11.69	0.11	7.56	4.97	7.96	68
20.93	0.10	4.24	20.7	28.56	80
26.63	0.13	3.33	100	183.2	61
27.65	0.20	3.22	2.74	7.52	40
29.40	0.13	3.03	5.38	9.86	61
33.30	0.40	2.69	1.26	6.90	20
36.60	0.10	2.45	9.18	12.61	83
39.50	0.11	2.27	6.58	10.56	72
40.36	0.40	2.23	1.66	9.11	21
42.50	0.20	2.12	3.16	8.68	42
45.91	0.20	1.97	2.13	5.84	42
50.20	0.08	1.81	9.39	10.75	10
55.12	0.40	1.66	1.15	6.32	22
60.00	0.13	1.54	4.67	8.56	68
68.27	0.26	1.37	3.10	11.34	35
80.01	0.48	1.18	1.1	10.23	21
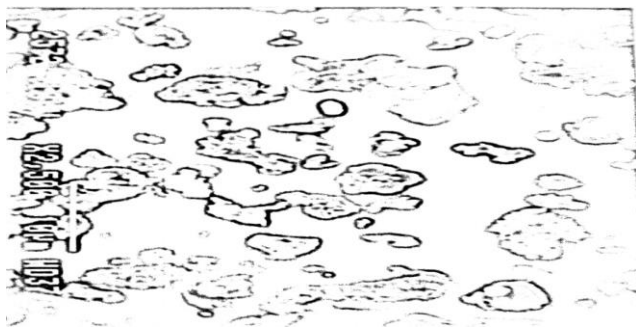
Fig 6. SEM micrograph f fly ash
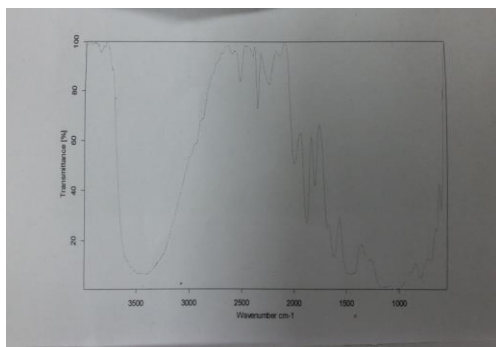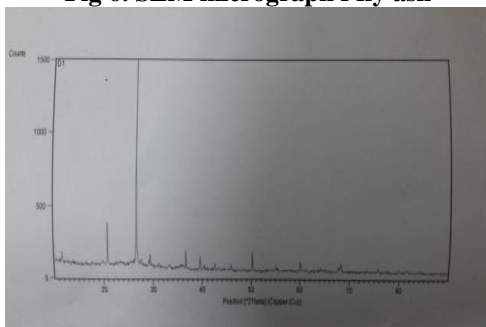
Fig 7. X-ray diffraction pattern and FTIR Spectra of Fly ash.

Conclusion

This study indicates that the adsorption experiment is a physical process. This means that the adsorption process obtained is a physical separation process and the adsorbed phenyl is simply but effectively removed from the aqueous solution (one phase) and transferred to fly ash (anotherphase).The fly ash now contains the Phenyl. Here the Chemicals characteristics of the adsorbed phenyl did not change; hence the use of adsorption technique in removing phenyl from aqueous solution is associated with its removal from aqueous solution and transfer to the flyash. Fly ash is capable of removing phenyl from aqueous solution. The adsorption of phenyl to fly ash is better fitted Freundlich Isotherm.

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