# An Alternative Cost Effective Method For Adsorption of Phenols in Effluents From Oil Refineries.

By

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A DISSERTATION SUBMITTED TO THE AVINASHILINGAM INSTITUTE FOR HOME SCIENCE AND HIGHER EDUCATION FOR WOMEN - DEEMED UNIVERSITY, COIMBATORE - 641 043

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# Introduction

# 1. INTRODUCTION AND OBJECTIVES

## 1. 1 INTRODUCTION

The quality of water is of vital concern for mankind, since it is directly linked with human welfare. Industrial waste contributes to the major source of various kinds of organic pollution in natural waters. While a huge amount of water is required for different industrial processes, only a small fraction of the same is incorporated in their products and lost by evaporation ; the rest find its way into the water courses as waste water, thus contributing to 'Pollution' of natural water bodies (Rao and Dhatta, 1987).

Occurrence of these pollutants is on the increase and several of them like phenols are not removed in conventional waste water treatment processes and pose problems such as odour, toxicity, foaming etc. and are a major obstacle to water reuse. Hence, the demand for more stringent control and protection of our water resources from pollution has mounted steadily in recent years.

The growth in demand for clean water has thus placed a heavy demand on the concept of water reuse. Numerous articles have been reported recently on the engineering feasibility of water reuse systems . Complete removal, or in some cases, reduction of the persistent organic compounds, to an acceptable concentration has become a major concern of advanced, water and waste water technology.

Phenols and other phenolic compounds are the mark of industrial pollution and are of particular concern in waters used for drinking water supplies, since on chlorination they may produce the odoriferous bad tasting chlorophenols (Jorgenson, 1979) . These phenolics are not present in natural waters but are contributed by the effluents from oil refineries (Manivasagam, 1985), Steel mills, gas works, coke plants, chemical plants, tar and petroleum industries, in the manufacture of stone and glass wool and in coal distillation plants. Thus the removal of phenolic tastes and odours from a water supply is a serious challenge to water engineers and water chemists.

## 1. 2 OBJECTIVES OF THE STUDY

- To effectively adsorb phenol in water using cheap sources.
- To reduce the time of treatment of waste water.
- To find the optimum pH at which maximum adsorption is seen.
- To find the optimum dosage of carbon and flyash, required for maximum adsorption
- To determine the optimum contact time for effective adsorption of phenols.
- To reduce the cost of treatment of waste water.
- To effectively use a pollutant - Flyash, in the removal of a pollutant - Phenol.

# Review of Literature

# 2. REVIEW OF LITERATURE

## 2.1 EFFECTS OF PHENOL IN EFFLUENTS

Discharge of raw waste water from industries having high concentration of phenolics, imposes serious effects on aquatic life.

The life of a stream may undergo a fundamental change if phenolic waste water is introduced into it. It has been found that animal plankton are even more sensitive to phenol, than fish. (Nowacki et.al. 1953)[28]. The $LD_{50}$ (mg per lit) at which half the experimental animals will die is 10mg/litre and the toxicity limit is 3 mg/litre (Kemp.et.al.1973)[28]. Apart from the toxic effect of phenols, their presence in rivers, impart odour and taste to the flesh of fish. As little as 1 mg/lit of phenol, causes deterioration in the taste of fish meat. If chlorophenols are present, this value falls even below 0.1 mg per litre (Jorgenson, 1979).

Phenol exerts a BOD of about two pounds Oxygen per pound phenol. The theoretical oxygen demand is 2.38 lb oxygen/lb.phenol[9] and must be therefore removed before discharge.

Further more, a pronounced and undesirable effect is displayed by phenols on potable water. Concentrations as small as 0.1-0.2 mg/lit may be detected by taste.

The standards for, composition of drinking water for phenols and for disposal of waste water highlights, that the maximum permissible level of phenol in potable water is 0.002mg/lit (WHO , 1971) (Table 1) and that for industrial waste water has been figured in Table 2.

## 2. 2 ENVIRONMENTAL IMPACT OF OIL REFINERY EFFLUENTS

Increasing demand of liquid fuel and other petroleum products has compelled setting up of oil refineries in several parts of the country, and thus the number of oil refineries in India has increased substantially. But while most of the earlier refineries are located near the seashore, many of the new installations are located far away from the sea and discharge their waste water to the inland water courses. As such pollution potential of the refinery waste has gone up considerably and demands a careful attention.

Refineries are usually large installations with a complex series of operations. The processing operations, that are the principal sources of waste are : Storage and transportation of crude oil, Crude oil desalting fractionation, cracking, molecular rearrangement and refining. Generally 10-20m3 of effluent are discharged for every ton of petroleum processed, if the water is recycled.

The characteristic feature of the effluent are: free and emulsified oil, phenolic compounds in varying concentrations, sulphurous compounds, BOD loading and suspended solids (Table 3) (Balasubramaniam, 1992).

A typical analysis of the waste water from an oil refinery is depicted in Table 4, and a waste water profile of a petroleum refinery in Table 5. The analytical data for waste water from an oil refinery after a three step treatment is given in Table 6.

It is seen that after flocculation - one of the treatment steps, there is 64 mg/lit of phenol which can be effectively removed by adsorption on activated carbon.

One of the major water management problems is the lack of adequate quantitative data to facilitate the selection of an optimum phenol removal strategy. The selection of the most suitable methods and the sequences of the treatment processes depends not only on the raw waste characteristics but also on the desired effluent quality specified by local authority. The raw waste characteristics also vary from one refinery to another. The nature of pollutants depends not only on the refining process but also on the quantity of crude oil. All these aspects are to be considered in the design of the treatment units of a refinery waste.

## 2.3 METHODS OF TREATMENT OF WASTE WATER CONTAINING PHENOLS

Various methods have been envisaged for the treatment of effluents containing phenols. These include mechanical treatments, coagulation, activated sludge treatments, biological oxidation, extraction, Poll-Hilckens stock method and adsorption on activated carbon.

Treatment of refinery waste water is done in three steps (Rao and Dhatta, 1987):

- Physical separation of free oil
- Chemical coagulation of emulsified oil
- Biological treatment for removal of phenol, BOD and other toxic materials.

- In the biological treatment waste stabilisation ponds require large area, but are capable of reducing phenol by 61-99%, with a retention period of 60 days.

- Mechanical treatments and coagulation has no effect and slow filtration does not eliminate these products completely (Degremont, 1972).

- Treatment of refinery waste by activated sludge process is affected, when the oil concentration exceeds about 30mg/l (Rao and Dhatta, 1987). Chakravarty and Bhaskaran observed that activated sludge treatment of chemically treated refinery waste results in very poor removal of BOD and phenol.

- In activated sludge treatment a biological culture adopted to waste water must be used and phenol oxidising bacteria must be present. It has been found that it is possible to oxidise phenol but it is necessary to acclimatise the activated sludge plant. Also a long time and large investment are other necessities.

- A two-step biological treatment of $1000m^3$ waste water/24 hour, with a phenol concentration of 500 mg per lit will require an expenditure as high as $500.000 (Jorgenson, 1979). The waste water considered in this case has a $BOD_5$ more than $300 which is slightly higher than the corresponding investment for the biological treatment of municipal waste water.

- Plants for tar distillation are often smaller than coke works and since phenol extraction plants and biological treatment plants require larger investments, it will not be possible for smaller tar distillation plants to solve their waste water problems. Similarly in the treatment of waste water from the production of oil refineries, stone and glasswool, the biological extraction process will be relatively more expensive.

- Solvent extraction is another method made use in the recovery of phenols from effluents. The method is however capital intensive and the costs increase quickly, when high phenol removal efficiencies are required.

- Owing to the disadvantages seen in the above stated methods, adsorption has been advocated as the most promising among the currently known methods for removal of phenol from waste waters.

Thus, all the above lines in the treatment of waste waters are relatively expensive and time consuming, requires more labour, when compared to the effective means of removal of phenols by adsorption on activated carbon obtained from Coirpith, and Flyash; both of which are cheap and of greater availability.

## 2.4. SIGNIFICANCE OF ADSORPTION USING ACTIVATED CARBON FROM COIRPITH, AND FLYASH IN THE EFFECTIVE REMOVAL OF PHENOLS

Numerous Unit operations have been evaluated for their efficiency, in the removal of organic pollutants. To date, the most widely utilised treatment process for removing undesirable organic matter from polluted waters have been activated carbon adsorption.

The concept of adsorption of organic materials onto carbon is not new. As early as 1883, Charcoal filters were employed in the United States to remove taste and odour from a water supply (American Water Works Association, 1971)

Adsorption on activated carbon has been found superior to other techniques because of the high quality effluent achieved, simplicity of design, ease of operation and insensitivity to toxic substances (Martin et.al)[20]. It increases the coagulation power of the process and is the safest means of purifying drinking water, industrial process water and certain waste waters. Also no skilled personnel are required in the treatment process.

Activated charcoal is a carbon material with a highly developed porous structure and a large internal specific surface area. Granular and powdered activated carbon adsorption is finding expanded application, as an advanced treatment process for the removal of low concentration of soluble organic material. In oil refineries it is being used as a means of removing low concentrations of phenols and trace organic molecules, that might have toxic effect on water supplies.

Because of the relatively low solubility in aqueous solution, phenols are easily adsorbed by activated carbon. It has been found that phenols can be adsorbed by various kinds of granular carbon even if the carbon is already exhausted for removal of organic matter (Degremont, 1972). The extent of removal of phenols in water varies with the type of phenol, dosage, type of carbon, pH and concentration of the medium.

The present investigation is carried out with activated carbon from coirpith and with Flyash. Coir pith is an agricultural waste found in abundance and thus considerably reduces the cost of effluent treatment process.

Flyash is a pollutant of thermal power stations with greater availability. Thus both adsorbents used in present study are cheaper sources and can be effectively used in the treatment of Oil refinery effluents.

### 2.4.1 UTILISATION OF FLYASH IN ADSORPTION STUDIES

Flyash is the pulverised fuel ash obtained as a fine particulate mineral residue left behind, after all the combustibles in the coal. Literally flyash may have more or less the same composition of coal ash but differs in mineralogy and morphology. It is a waste product of thermal power plants and is a suitable economic alternative in waste water treatment.

By 2000 A.D. India is likely to produce about 70 million tonnes/year of flyash causing serious problems of disposal and environmental pollution. In India annual production of flyash, from different thermal power plants is over 25 million tonnes/year. Presently, major portion of flyash remains unutilised. The effective bulk consumption and economic disposal of flyash is attracting considerable attention of many scientists. Thus utilisation of Flyash for eco-friendly purposes is now picking up fast in several countries including India.

This work also investigates the recent interest in the utilisation of flyash for phenol removed as an unconventional and low-cost adsorbent.

# Materials and Methods

# 3. MATERIALS AND METHODS

The adsorbents employed in the present study are, activated carbon from coir pith, and flyash obtained from Tuticorin Thermal Power Station. The characteristics of the Flyash are listed in Table 7.

## 3.1 PROJECT PLAN

Batch studies were conducted at room temperature to estimate the potentiality of activated carbon and flyash in effective removal of phenols from effluents. The batch technique was selected because of its simplicity and ease of evaluating the parameters which influence the adsorption process. The agitation speed was taken almost constant for all experiments to study the effect of various parameters on phenol removal. All reagents used were of AR grade.

## 3.2 PARAMETERS STUDIED

i. Carbon production from Coir pith

ii. Activation of carbon

iii. Determination of optimum pH at which maximum adsorption is seen.

iv. Determination of optimum contact time for maximum phenol removal.

v. Determination of optimum carbon and flyash dosage.

vi. Comparison of the effectiveness of activated carbon and flyash in adsorption of phenols.

vii. Application of results to fit into Langmuir and Freundlich isotherms.

## 3.3 SELECTION OF SAMPLE

The present study was carried out with a synthetically prepared effluent which has similar composition as that of a typical oil refinery effluent (Table-6). Only pH and amount of phenol, were taken into account in the preparation of the synthetic effluent. Oil refinery effluents contain significant amounts of phenol and other phenolic compounds like cresol, catechol etc. Owing to the difficulty in the estimation of all the phenolic compounds, after adsorption, a synthetic effluent which consisted of only phenol was used.

## 3.4 CARBON PRODUCTION

The carbon used for the study was obtained from coir pith. The coir pith was washed well with distilled water several times, and dried for 10 hours at 120°C.

For every 10 grams of coir pith 15 ml of concentrated sulphuric acid was added and maintained for 10 hours. The carbon so produced was washed several times with distilled water and dried at 150°C for 10-12 hours.

### 3.5 ACTIVATION OF CARBON[20]

The carbon so produced was heated with anhydrous zinc chloride in the ratio of 10:1, in a silica dish for one hour in closed condition, after which the carbon was washed with distilled water, dried at 120°C for 10 hours and received through a 250 mesh.

### 3.6 ANALYTICAL METHODS

Phenol concentrations were assessed by Folin-Ciocalteau method (Otto Folin and W.Dennis, 1915) in a Systronics Digital colorimeter. The procedure is given in Appendix 1.

### 3.7 TREATMENT OF EFFLUENT AND STUDY OF VARIOUS PARAMETERS

The effluent was treated with the activated carbon, in stoppered pyrex bottles and placed in a horizontal bench shaker for a certain period of time. Then the solutions were filtered through Whatman filter paper No.42 to remove the used adsorbent. The clear solution was then estimated for its residual phenol concentration as in Appendix 1. Similar procedure was carried out with flyash. Various parametes like pH, contact time and dosage variation were studied at fixed concentrations.

### 3.7.1 DETERMINATION OF OPTIMUM CARBON AND FLYASH DOSAGE IN THE EFFECTIVE ADSORPTION OF PHENOLS

100 mg. of activated carbon was added to 50 ml of the effluent containing 9 mg of phenol and shaken in a horizontal bench shaker at room temperature, for 60 minutes, after which, the solution was filtered and residual phenol concentration determined as in Appendix 1. Similar procedure was repeated with 300,500, 700, 900 and 1000 mg of activated carbon and 1, 5, 10, 15 and 20g of Flyash.

The amount of adsorption was computed from the difference between the initial concentration and the equilibrium concentration of the adsorbent.

### 3.7.2 DETERMINATION OF OPTIMUM pH AT WHICH MAXIMUM ADSORPTION OF PHENOLS IS SEEN.

The optimum pH was determined by laboratory runs at pH 1,3,5,7 and 9. 200mg of activated carbon was added to 50 ml of effluent of varied pH and shaken for 60 minutes at room temperature in a horizontal bench shaker, after which the solutions were filtered and residual concentration of phenol determined by Folin Ciocalteau method as in Appendix 1. Similar procedure was repeated with 5g of Flyash.

The pH of the solutions were checked with a digital pen-type pH meter. The pH values were adjusted by addition of hydrochloric acid and sodium hydroxide.

### 3.7.3 DETERMINATION OF OPTIMUM CONTACT TIME AT WHICH MAXIMUM ADSORPTION OF PHENOLS IS SEEN

500 mg of activated carbon was added to 50 ml of the effluent containing 9 mg of phenol and shaken in a horizontal bench shaker at room temperature. The residual phenol concentration was determined at varying contact times of 10, 20, 30, 40, 50 and 60 minutes, after filtration through Whatman filter paper No.42.

Similar procedure was repeated with 5g. of flyash and contact time varied as 1, 2, 3, 4, 5 and 6 hours.

# Results And Discussion

# 4. RESULTS AND DISCUSSION

## 4.1 RESULTS

The results of the adsorption of phenols present in the synthetic effluent, onto activated carbon obtained from coir pith, and flyash have been tabulated and figured.

## 4.2 DISCUSSION

### 4.2.1 DEPENDANCE OF EFFICIENCY ON QUANTITY OF ADSORBENT - EFFECT OF DOSAGE VARIATION

It was seen from the study that adsorption rate is increased by increasing the dosage of adsorbent. Upto a dosage of 500 mg of activated carbon (Fig.1) it is seen that adsorption rate is sharply increased by increasing the dosage from 100 mg to 500 mg (44.1% to 95.1%). After 500mg the adsorption increases steadily upto 99.66% for 1 g of activated carbon.

With Flyash, there is a steady increase in the adsorption rate from 1 g of Flyash upto 20g. No sharp increase is seen in adsorption rate as in the case of activated carbon.

From the above results it is seen that 1g of activated carbon and 20g of Flyash are required for the maximum removal of phenol. The availability of more adsorption sites, for adsorption of phenols on increasing the dosage of activated carbon, contributes to the increase in the adsorption rate.

The ability of activated carbon to remove soluble organics from waste water is a consequence of the similarity in surface chemistry between activated carbon and organic molecules. The efficient adsorption of activated carbon may be attributed to its large interfacial area due to pores or channels throughout the particles. The activation step gives a complex network of irregularly shaped and partially connected passages. Activated carbon usually carries a net surface charge that is slightly negative (Donald.W. Sundstrom, 1979 ). The surface charges depend upon the source of the carbon and the activation procedure.

The removal mechanism in the case of flyash is due to chemical coagulation with metallic oxides like $Al_2O_3$, $Fe_2O_3$, CaO, $SiO_3$ and MgO.

The major constituents of Flyash are silica and alumina. Silica contains oxygen bridges between Silicon atoms. The central ion of silicates, $Si^{++}$ atom , has a very strong affinity for electrons. Since oxygen atoms bound to silicon ion have a very low basicity, it causes the silica surface to act as a very weak acid. The oxygen atoms on the silica surface are free to react with water forming surface silanol groups. Silica content thus plays a important role in the adsorption of cations and of heavy metal ions.

### 4.2.2 EFFECT OF pH VARIATION

From Tables 12 and 13 and Figures 5 and 6 it is seen that adsorption rate is dependent on pH. Table 12 portrays the increase in adsorption, as the pH is increased from 1.2 to 3.3 (74% to 78%) and then decreases upto 7.2. Maximum removal of phenol is seen at a acidic pH of 3.3. At the alkaline pH of 11.4, no colourant was produced and estimation of phenol was not possible.

Also a minimum pH of 1.2 was selected because below this, there is a nil feasibility in estimation of residual phenol due to lack of colour formation with reagent. With flyash, a very small increase in adsorption rate is noted at an acidic pH.

Maximum removal of phenol is seen at pH 1.3 (16.67%), after which upto pH 9.0 there is decrease in % removal.

Neutralisation of the charges on carbon may take place by hydrogen ions which make more of the surface accessible for adsorption. Hence maximum removal is seen in acidic pH.

### 4.2.3 EFFECT OF CONTACT TIME

From the results it is seen that at the initial stage, adsorption of phenols onto activated carbon is very fast and more than 85% adsorption has occurred in the first 15 minutes(Fig.3).

After 20 minutes the adsorption rate showed steady increase and 98.66% removal is obtained after 60 minutes, which is sufficient for obtaining maximum removal. With Flyash as adsorbent, it is seen that maximum removal (15.5%) is obtained with contact time as 6 hours.

Also there is no sharp increase in adsorption rate at the start, rather, a progressive increase in % removal is noted.

The instantaneous utilisation of the most readily adsorbing sites on the adsorbent surface is the cause for the sharp increase in the adsorption rate, at the first 15 minutes itself.

### 4.2.4 ADSORPTION ISOTHERMS

#### 4.2.4.1. APPLICATION OF RESULTS OF DOSAGE VARIATION OF ADSORBENT IN TERMS OF LANGMUIR ADSORPTION ISOTHERMS

The results obtained in the study of dosage variation of the adsorbent, was interpreted in-terms of Langmuir and Freundlich Isotherms. The purpose was to provide a means by which the influence, which the dosage variation parameter exhibited, on adsorption process, could be evaluated.

Langmuir Adsorption Isotherm is based on the assumption that points of valency exist on the surface of the adsorbent and that, each of these sites is capable of adsorbing one molecule. Thus the adsorbed layer, will be one molecule thick. Further it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbent and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site.

The Langmuir Adsorption Isotherm is commonly given by

$$\frac{x}{m} = \frac{abc_e}{1+ac_e} \quad \text{where}$$

$x$ - amount of phenol adsorbed (mg)

$m$ - weight of adsorbent (mg)

$c_e$ - concentration of phenol remaining after adsorption

$a,b$ - constants

On rearranging,

$$\frac{1}{x/m} = \frac{1}{b} + \frac{1}{abc_e}$$

The linear form of Langmuir Isotherm at room temperature is plotted between $1/(x/m)$ versus $1/c_e$ for different doses of the adsorbent for initial phenol concentration of 180 mg/l. 1/b and 1/ab are evaluated from the intercept and slope respectively.

From Fig.7 it is seen that a best fit line with slope 41.139 (mg dose/mg phenol) and intercept 52.2301 (mg dose) is obtained with the adsorbent as activated carbon. From Fig.8 it is seen that a best fit line with slope 1381.39 (g dose/mg phenol) and intercept -3.4838 (g dose) is obtained with flyash as adsorbent.

These linear plots show the applicability of Langmuir model in present system, indicating the formation of monolayer coverage of adsorbate on the surface of adsorbent.

### 4.2.4.2 FREUNDLICH ADSORPTION ISOTERM

Attempts were made to fit the data of dosage variation of adsorbent into Freundlich Isotherm (Table 16 and 17).

The equilibrium data at room temperature has been processed in accordance with Freundlich Isotherm, given by the equation,

$$\log x/m = \log K + 1/n \log c_e$$

Freundlich Isotherm has been illustrated to be a special case of heterogeneous surface energy and it can be easily extended to this case.

The linear form of Freundlich Isotherm at room temperature is plotted between log x/m versus log $c_e$ for different doses of the adsorbent , for initial concentration of 180 mg/l. K and 1/n are evaluated from the slope and intercept respectively.

The Freundlich adsorption parameter reflect the following :

From Fig. 9 it is seen that the values for K and 1/n for phenols are 0.009014 (mg/dose) and 0.29838 (mg/mg phenol) respectively showing the best adsorption character of activated carbon. With flyash as adsorbent the values of K and 1/n are 0.007226 (g/dose) and 1.5848 (g/mg phenol) respectively, portraying the low efficiency of Flyash in removal of phenols (Fig. 10).

The higher values of K for activated carbon shows that it is a better adsorbent than flyash. The values of n between 2 - 10 implies good adsorption characteristics (Mc.kay et. al., 1980). This is true for activated carbon and not for flyash.

## 4.2.5. APPLICATION OF THE METHOD OF LEAST SQUARES TO THE LANGMUIR AND FREUNDLICH ISOTHERMS TO OBTAIN A BEST FIT CURVE

To obtain best fit curves for the adsorption isotherms the method of least squares was made use of. A model of best fit curve with Table.14 is given below

Let $\mathbf{1/c_e = X}$

$\mathbf{1/x/m = Y}$

| X | Y | $X^2$ | XY |
|---|---|---|---|
| 0.0094 | 27.027 | $8.83 \times 10^{-5}$ | 0.2540 |
| 0.0385 | 39.060 | $1.482 \times 10^{-3}$ | 1.5038 |
| 0.1155 | 58.487 | $1.334 \times 10^{-2}$ | 6.7544 |
| 0.2778 | 79.370 | $7.717 \times 10^{-2}$ | 22.0490 |
| 0.3846 | 101.010 | $14.791 \times 10^{-2}$ | 38.8484 |
| 1.6700 | 111.110 | 2.790 | 185.5537 |
| 2.4958 | 416.051 | 3.0289 | 254.9634 |

Substituting in the equations

$\Sigma y = na + b\Sigma x$

$\Sigma xy = ax + b\Sigma x^2$

We get,

$$416.0510 = 6a + 2.4958b$$

$$254.9634 = 2.4958a + 3.02896b$$

On solving, a = 25.665 and b = 41.107. The values of a and b are substituted in equation

$$\mathbf{y_1 = a + bx}$$

A plot of $y_1$ and x gives a best fit curve from which the slope b and intercept a can be evaluated.

Thus, by the method of least squares, best fit curves were obtained for the adsorption isotherms (figures 7,8,9 and 10).

The values have been incorporated in Tables 14,15,16 and 17. The slopes and intercepts have been evaluated from the figures and given in Table 18.

### 4.2.5 COMPARISON OF THE EFFECTIVENESS OF FLYASH AND ACTIVATED CARBON IN THE REMOVAL OF PHENOLS

It is seen from the results that activated carbon is more efficient and a far better adsorbent than flyash.

Maximum removal of phenol is seen with 1 g of activated carbon, while to achieve the same phenol removal, approximately sixty seven times more Flyash would be required. Also the contact time for maximum removal of phenols with activated carbon as adsorbent is 60 minutes while to achieve 30% removal a contact time of 10 hours is required with Flyash as adsorbent. Thus time consumption is very high in the case of Flyash.

It is seen from the study of pH variation that just 200 mg of activated carbon is sufficient to induce 78% removal of phenol at an acidic pH of 3.3. No notable increase in percent removal is seen in the case of Flyash.

From Freundlich Isotherm it is seen that the 'n' values for phenols with activated carbon is greater than that obtained for Flyash, thus showing greater suitability of activated carbon for adsorption of phenols.

# Summary and Conclusion

# 5. SUMMARY AND CONCLUSION

The following significant conclusions could be drawn on the basis of present work :

- % removal of phenol was found to increase with increase in dosage variation with initial concentration being constant.

- % removal of phenol is pH dependent and is found to increase with decreasing pH and maximum removal is noted at pH 3.3.

- Maximum removal is seen with contact time as 60 minutes for activated carbon and 10 hours for flyash.

- From the results it can be concluded that activated carbon is highly efficient than flyash, though flyash is more economical and requires no production.

- It can be concluded that activated carbon for practical use in waste water treatment can be produced from coirpith by means of chemical activation with sulphuric acid and anhydrous zinc chloride. 1g of activated carbon is found to be sufficient for getting maximum removal (99.66%) of phenol, with contact time as 60 minutes. This quantity of adsorbent required is less in acidic conditions (pH 3.3).

- The quantity of flyash required for adsorption of phenols can be considerably reduced by impregnation of Flyash with Aluminium hydroxide or ferric hydroxide, where by the lone pair of electrons of phenols and Lewis acid sites ($Fe^{3+}$, and $Al^{3+}$) on impregnated Flyash undergo complexation, thus increasing the adsorption capacity of flyash.

In summary, the technical feasibility of removing phenolic compounds from aqueous solution via activated carbon adsorption is excellent. High adsorptive capacities are the rule, rather than exception, for phenols.

## TABLE - 1

## STANDARDS FOR COMPOSITION OF DRINKING WATER FOR PHENOLS

| | U.S. Public Health (mg/lit) | WHO 1971 | By ministry of works and Housing (1975) |
|---|---|---|---|
| Highest desirable | . | 0.001 | 0.001 mg/lit - Acceptable |
| Maximum | 0.001 | 0.002 | 0.002 mg/lit - Cause of Rejection |

**( Trivedy and Goel, 1986).**

## TABLE - 2

## ISI STANDARDS FOR DISPOSAL OF WASTE WATER

| **Tolerance limit for phenols:** |
|---|
| (i) Discharge of Industrial waste water in<br>- inland surface water 1.0 mg/lit<br>- public services 5 mg/lit |
| (ii) For inland surface water when used as raw water for public water supplies and bathing ghats (1974) : 0.005 mg/lit |

**TABLE - 3**

CHARACTERISTICS OF OIL REFINERY WASTE

| **Characteristic** | **mg/lit** |
|---|---|
| FreeOil | 2000 - 3000 |
| Emulsified Oil | 90 - 120 |
| $H_2S$ & RSH | 10 - 220 |
| Phenolic Compounds | 12 - 30 |
| $20^0C$ $BOD_5$ | 100 - 300 |
| Suspended Solids | 200 - 400 |

**( Rao and Dhatta, 1987 )**

## TABLE - 4

## A TYPICAL COMPOSITION OF WASTE WATER FROM AN OIL REFINERY

| | | |
|---|---|---|
| pH | : | 6.5 - 8.4 |
| Alkalinity mg/l | : | 120 - 3000 |
| Permanganate value mg/l | : | 100 - 1000 |
| BOD mg/l | : | 100 - 1000 |
| Organic Carbon (mg/l Carbon) | : | 12 - 650 |
| Organic Nitrogen (mg/l N) | : | 4 - 10 |
| NH3 mg/l | : | 5 - 80 |
| TSS mg/l | : | 150 - 4000 |
| Volatile suspended solid mg/l | : | 150 - 4000 |
| Sulphurous Compounds | : | 20 - 80 |
| Phenol$^{+}$ (mg/lit) | : | 20 |
| Untreated Phenol$^{\$}$ (mg/lit) | : | 180 |

**+ A.K.De, 1995 .**

**$ Jorgenson, 1979.**

## TABLE - 5

## A TYPICAL PETROLEUM REFINERY WASTE WATER CHARACTERISTICS

## WASTE WATER PROFILE PER 1000 BARRELS OIL TAKEN OUT

| SOURCE | VOLUME | BOD | PHENOLS | SULPHIDE S lbs |
|---|---|---|---|---|
| Crude Oil Production and Storage | 400 | 1.0 | - | - |
| Desalting | 200 | 2.0 | 0.1 | 2.0 |
| Fractionation | 65,200 | 7.3 | 1.7 | 1.0 |
| Cracking | 29,000 | 14.5 | 15.4 | 0.6 |
| Molecular rearrangement | 7,000 | 0.1 | 0.1 | 1.7 |
| Refining | 35,800 | 53.9 | 5.2 | 0.7 |
| Total | 137,600 | 78.8 | 22.5 | 12.0 |
| Discharge from API separator | 150,000 | 204.5 | 16.9 | 5.6 |

**(Jorgenson, 1979 ).**

TABLE - 6

ANALYTICAL DATA FOR WASTE WATER FROM AN OIL REFINERY AFTER A THREE-STEP TREATMENT (mg/l)

| | Untreated Water | After Separation | After Flocculation | After Biological Treatment |
|---|---|---|---|---|
| BOD | 860 | 680 | 200 | 20 |
| COD | 1880 | 1600 | 400 | 40 |
| S | 40 | 36 | 12 | 0 |
| PHENOL | 180 | 170 | 64 | 0.5 |

(Jorgenson, 1979).

TABLE - 7

CHARACTERISTICS OF FLYASH OBTAINED FROM

TUTICORIN THERMAL POWER STATION

| | Magnitude % by weight |
|---|---|
| $SiO_2$ | 53.4 |
| $Al_2O_3$ | 24.6 - 23.8 |
| $Fe_2O_3$ | 3.8 - 4 |
| CaO | 7.2 |
| MgO | 3.3 |
| LOI 800$^{o}$C | 1.5 |
| Total (% of FA) | 100.2 - 99.4 |
| Specific gravity | 2.3 g/cc |
| Surface area | 300 mesh |

## TABLE - 8

## PERCENTAGE REMOVAL OF PHENOL WITH DOSAGE VARIATION OF ACTIVATED CARBON

CONDITION : 'y' mg of activated carbon shaken with 50ml effluent at room temperature

pH : 7.4

CONTACT TIME : 60 minutes

| S.No. | Initial Amount of phenol mg/50ml effluent | 'y' mg of Activated carbon | Final amount phenol mg/50ml ($c_e$) | mg of phenol adsorbed (x) | % removal of phenol |
|---|---|---|---|---|---|
| 1. | 9 | 100 | 5.30 | 3.70 | 44.11 |
| 2. | 9 | 300 | 1.30 | 7.70 | 85.56 |
| 3. | 9 | 500 | 0.43 | 8.57 | 95.10 |
| 4. | 9 | 700 | 0.18 | 8.82 | 98.00 |
| 5. | 9 | 900 | 0.13 | 8.87 | 98.60 |
| 6. | 9 | 1000 | 0.03 | 8.99 | 99.66 |

TABLE - 9

PERCENTAGE VARIATION OF PHENOL WITH

DOSAGE VARIATION OF FLYASH

CONDITION : 'y' grams of flyash shaken with 50ml effluent at room temperature

pH : 7.4

CONTACT TIME : 10 hours

| S.No. | Initial Amount of phenol mg/50ml effluent | 'y' grams of flyash | Final amount phenol mg/50ml ($c_e$) | mg of phenol adsorbed (x) | % removal of phenol |
|---|---|---|---|---|---|
| 1. | 9 | 1 | 8.78 | 0.22 | 2.40 |
| 2. | 9 | 5 | 8.00 | 1.00 | 11.11 |
| 3. | 9 | 10 | 7.20 | 1.80 | 20.00 |
| 4. | 9 | 15 | 6.90 | 2.10 | 23.30 |
| 5. | 9 | 20 | 6.30 | 2.70 | 30.00 |

TABLE - 10

PERCENTAGE REMOVAL OF PHENOL WITH CONTACT TIME

CONDITION : 500 mg of activated carbon shaken with 50ml effluent at room temperature

pH : 7.4

| S.No. | Initial Amount of phenol mg/50ml effluent | Contact time (min) | Final amount phenol mg/50ml ($c_e$) | mg of phenol adsorbed (x) | % removal of phenol |
|---|---|---|---|---|---|
| 1. | 9 | 10 | 1.30 | 7.70 | 85.50 |
| 2. | 9 | 20 | 0.27 | 8.73 | 97.03 |
| 3. | 9 | 30 | 0.16 | 8.84 | 98.20 |
| 4. | 9 | 40 | 0.14 | 8.86 | 98.40 |
| 5. | 9 | 50 | 0.13 | 8.87 | 98.50 |
| 6. | 9 | 60 | 0.12 | 8.88 | 98.66 |

## TABLE - 11

## PERCENTAGE REMOVAL OF PHENOL WITH CONTACT TIME

CONDITION : 5g of flyash with 50 ml effluent

pH : 7.4

| S.No. | Initial Amount of phenol mg/50ml effluent | Contact time (hrs.) | Final amount phenol mg/50ml ($c_e$) | mg of phenol adsorbed (x) | % removal of phenol |
|---|---|---|---|---|---|
| 1. | 9 | 1 | 8.79 | 0.21 | 2.30 |
| 2. | 9 | 2 | 8.60 | 0.40 | 4.40 |
| 3. | 9 | 3 | 8.40 | 0.60 | 6.67 |
| 4. | 9 | 4 | 8.25 | 0.75 | 8.33 |
| 5. | 9 | 5 | 8.00 | 1.00 | 11.00 |
| 6. | 9 | 6 | 7.60 | 7.40 | 15.50 |

TABLE - 12

PERCENTAGE REMOVAL OF PHENOL WITH pH VARIATION

CONDITION : 200 mg of activated carbon shaken with 50ml effluent at room temperature

CONTACT TIME : 60 minutes

| S.No. | Initial Amount of phenol mg/50ml effluent | pH | Final amount phenol mg/50ml ($c_e$) | mg of phenol adsorbed (x) | % removal of phenol |
|---|---|---|---|---|---|
| 1. | 9 | 1.2 | 2.3 | 6.7 | 74 |
| 2. | 9 | 3.3 | 2.0 | 7.0 | 78 |
| 3. | 9 | 5.4 | 2.2 | 6.8 | 76 |
| 4. | 9 | 7.2 | 3.5 | 5.5 | 61 |
| 5. | 9 | 9.0 | 2.2 | 6.8 | 76 |

TABLE - 13

PERCENTAGE REMOVAL OF PHENOL WITH pH VARIATION

CONDITION : 5g of Flyash shaken with 50ml effluent at room temperature

CONTACT TIME : 3 hours

| S.No. | Initial Amount of phenol mg/50ml effluent | pH | Final amount phenol mg/50ml ($c_e$) | mg of phenol adsorbed (x) | % removal of phenol |
|---|---|---|---|---|---|
| 1. | 9 | 1.3 | 7.50 | 1.50 | 16.7 |
| 2. | 9 | 3.1 | 7.70 | 1.30 | 14.4 |
| 3. | 9 | 5.0 | 7.90 | 1.10 | 12.2 |
| 4. | 9 | 7.2 | 8.01 | 0.99 | 11.0 |
| 5. | 9 | 9.0 | 8.20 | 0.80 | 8.9 |

## TABLE - 14

## INTERPRETATION OF RESULTS IN TABLE 8 IN TERMS OF LANGMUIR ADSORPTION ISOTHERM

| S.No. | mg of activated carbon (m) | Initial weight of phenol mg/50ml | Final concentration of phenol in | | x weight of phenol adsorbed | x/m adsorbate adsorbed /unit wt. of activated carbon | 1/x/m [Y] | $1/c_e$ [X] | $X^2$ | X Y | Y' |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | mg/50ml ($c_e$) | mg/l | | | | | | | |
| 1. | 100 | 9 | 5.30 | 106.0 | 3.70 | 0.0370 | 27.03 | 0.0094 | $8.84 \times 10^{-5}$ | 0.254 | 52.6169 |
| 2. | 300 | 9 | 1.30 | 26.0 | 7.70 | 0.0256 | 39.06 | 0.0385 | $1.48 \times 10^{-3}$ | 1.504 | 53.8140 |
| 3. | 500 | 9 | 0.43 | 8.7 | 8.57 | 0.0171 | 58.48 | 0.1155 | $1.33 \times 10^{-2}$ | 6.7544 | 56.9820 |
| 4. | 700 | 9 | 0.13 | 3.6 | 8.82 | 0.0126 | 79.37 | 0.2778 | $7.77 \times 10^{-2}$ | 22.049 | 63.6590 |
| 5. | 900 | 9 | 0.13 | 2.6 | 8.87 | 0.0099 | 101.01 | 0.3846 | $14.79 \times 10^{-2}$ | 38.848 | 68.0500 |
| 6. | 1000 | 9 | 0.03 | 0.6 | 8.97 | 0.0090 | 111.11 | 1.6700 | 2.79 | 185.554 | 120.9330 |
| | | | | | | | 416.05 | 2.4958 | 3.0289 | 254.9634 | |

TABLE - 15

INTERPRETATION OF RESULTS IN TABLE-9 IN TERMS OF LANGMUIR ADSORPTION ISOTHERM

| S.No. | Grams of Flyash (m) | Initial weight of phenol mg/50ml | Final concentration of phenol in ($c_e$) | | x weight of phenol adsorbed (mg) | x/m adsorbate adsorbed/ unit wt. of flyash | 1/x/m [Y] | $1/c_e$ [X] | $X^2$ $\times 10^{-5}$ | XY | Y' |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | mg/50ml | mg/l | | | | | | | |
| 1. | 1 | 9 | 8.78 | 175.6 | 0.22 | 0.220 | 4.55 | 0.00569 | 3.237 | 0.0259 | 4.3763 |
| 2. | 5 | 9 | 8.00 | 160.0 | 1.00 | 0.200 | 5.00 | 0.00625 | 3.906 | 0.0310 | 5.1499 |
| 3. | 10 | 9 | 7.20 | 144.0 | 1.80 | 0.180 | 5.56 | 0.00694 | 4.816 | 0.0386 | 6.1030 |
| 4. | 15 | 9 | 6.90 | 138.0 | 2.10 | 0.140 | 7.14 | 0.00725 | 5.256 | 0.0518 | 6.5313 |
| 5. | 20 | 9 | 6.30 | 126.0 | 2.70 | 0.135 | 7.40 | 0.00794 | 6.304 | 0.0588 | 7.4844 |
| | | | | | | | | | $2.352 \times 10^{-5}$ | 0.2062 | |

TABLE - 16

INTERPRETATION OF RESULTS IN TABLE-8 IN TERMS OF FREUNDLICH ADSORPTION ISOTHERM

| S.No. | mg of activated carbon (m) | Initial weight of phenol mg/50ml | Final concentration of phenol in ($c_e$) | | x weight of phenol adsorbed | x/m adsorbate adsorbed/ unit wt of activ--ated carbon mg/mg | log x/m [Y] | log $c_e$ [X] | $X^2$ | XY | Y' |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | mg/50ml | mg/l | | | | | | | |
| 1. | 100 | 9 | 5.3 | 106.00 | 3.70 | 0.0370 | -1.4318 | 2.0253 | 4.1018 | -2.8998 | -1.4407 |
| 2. | 300 | 9 | 1.3 | 26.00 | 7.70 | 0.0256 | -1.5918 | 1.4150 | 2.0022 | -2.2523 | -1.6229 |
| 3. | 500 | 9 | 0.43 | 8.66 | 8.57 | 0.0171 | -1.7670 | 0.9378 | 0.8795 | -1.6570 | -1.7652 |
| 4. | 700 | 9 | 0.13 | 3.60 | 8.82 | 0.0126 | -1.8996 | 0.5563 | 0.3074 | -1.0567 | -1.8791 |
| 5. | 900 | 9 | 0.13 | 2.60 | 8.87 | 0.0099 | -2.0044 | 0.4150 | 0.1722 | -0.8318 | -1.9212 |
| 6. | 1000 | 9 | 0.03 | 0.60 | 8.97 | 0.0090 | -2.0458 | -0.2218 | 0.0491 | +0.4537 | -2.1112 |
| | | | | | | | | | 7.5144 | -8.2441 | |

TABLE - 17

INTERPRETATION OF RESULTS IN TABLE-9 IN TERMS OF FREUNDLICH ADSORPTION ISOTHERM

| S.No. | Grams of Flyash (m) | Initial weight of phenol mg/50ml | Final concentration of phenol in | | x weight of phenol adsorbed | x/m adsorbate adsorbed/ unit wt. of flyash mg/g. | logx/m [Y] | log $c_e$ [X] | $X^2$ | XY | Y' |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | mg/50ml ($c_e$) | mg/l | | | | | | | |
| 1. | 1 | 9 | 8.78 | 175.6 | 0.22 | 0.220 | -0.6576 | 0.9435 | 0.8902 | -0.6204 | -0.6459 |
| 2. | 5 | 9 | 8.00 | 160.0 | 1.00 | 0.200 | -0.6990 | 0.9031 | 0.8156 | -0.6313 | -0.7099 |
| 3. | 10 | 9 | 7.20 | 144.0 | 1.80 | 0.180 | -0.7447 | 0.8573 | 0.7349 | -0.6384 | -0.7826 |
| 4. | 15 | 9 | 6.90 | 138.0 | 2.10 | 0.140 | -0.8539 | 0.8388 | 0.7035 | -0.7163 | -0.8118 |
| 5. | 20 | 9 | 6.30 | 126.0 | 2.70 | 0.135 | -0.8697 | 0.7993 | 0.6388 | -0.6951 | -0.8754 |
| | | | | | | | | | 3.7832 | -3.3015 | |

TABLE - 18

VALUES OF THE SLOPES AND INTERCEPTS OF THE ADSORPTION ISOTHERMS.

| Figure | Slope 1/ab | | Intercept 1/b | |
|---|---|---|---|---|
| 7 | 41.139 | | 52.2301 | |
| 8 | 1381.390 | | -3.4838 | |
| Figure | Slope | | Intercept | |
| | 1/n | n | log k | k |
| 9 | 0.29838 | 3.35 | -2.0450655 | 0.009014 |
| 10 | 1.5848 | 0.60 | -2.1411773 | 0.007226 |

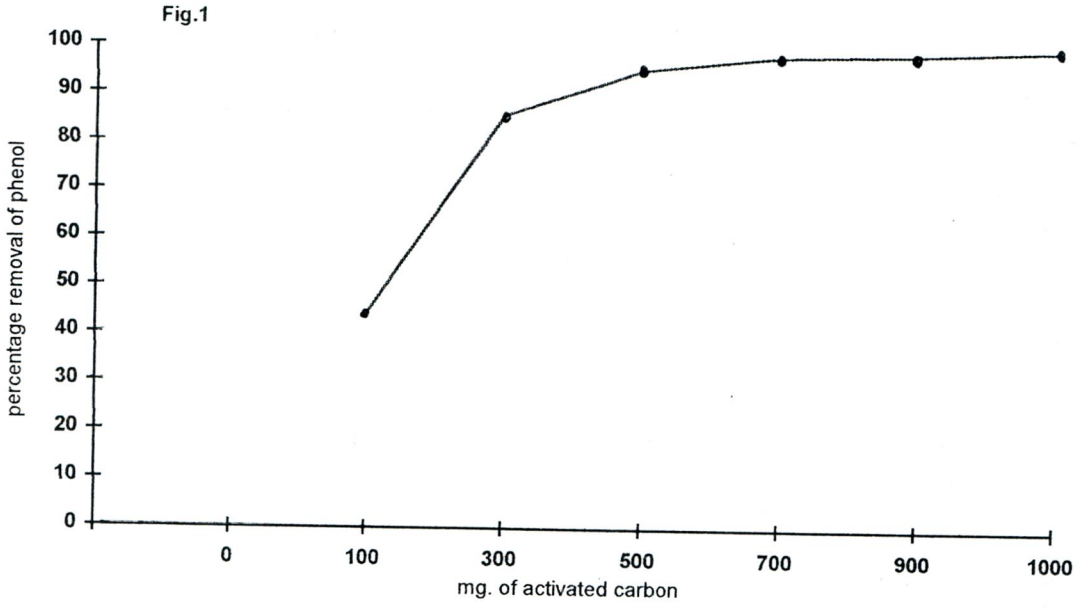



**FIG 1** : Variation of % removal of phenol with dosage of activated carbon

**CONDITION** : Y mg of activated carbon shaken with 50 ml . effluent at room temperature.

**CONTACT TIME :** 60 minutes

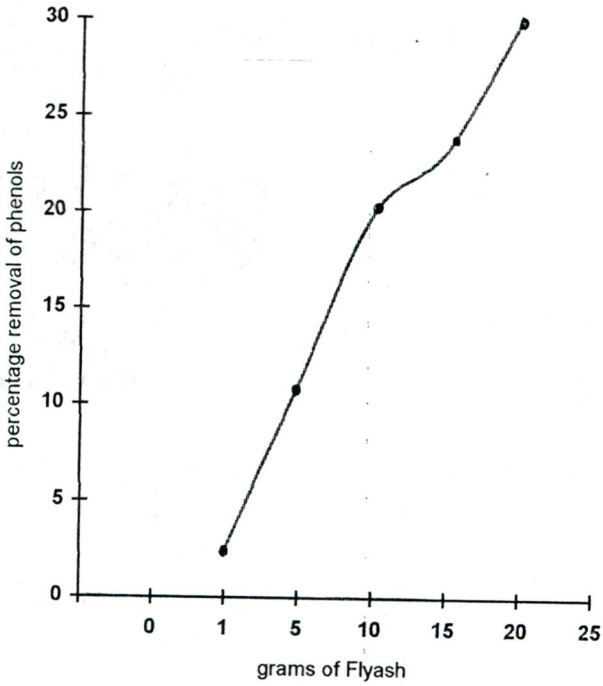



Fig.2

**FIG 2** : Variation of % removal of phenol with dosage of flyash

**CONDITION** : Y mg of flyash shaken with 50 ml . effluent at room temperature.

**CONTACT TIME** : 10 hrs.

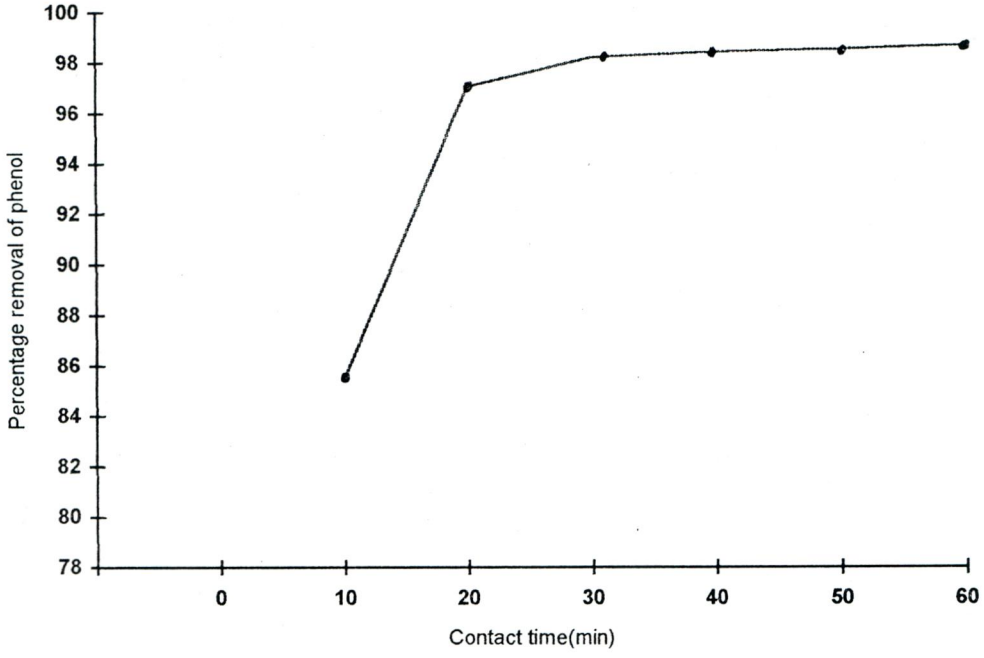



Fig.3

**FIG 3** : Variation of % removal of phenol with contact time.

**CONDITION** : 500 mg of activated carbon shaken with 50 ml . effluent at room temperature.

**pH** : 7.6

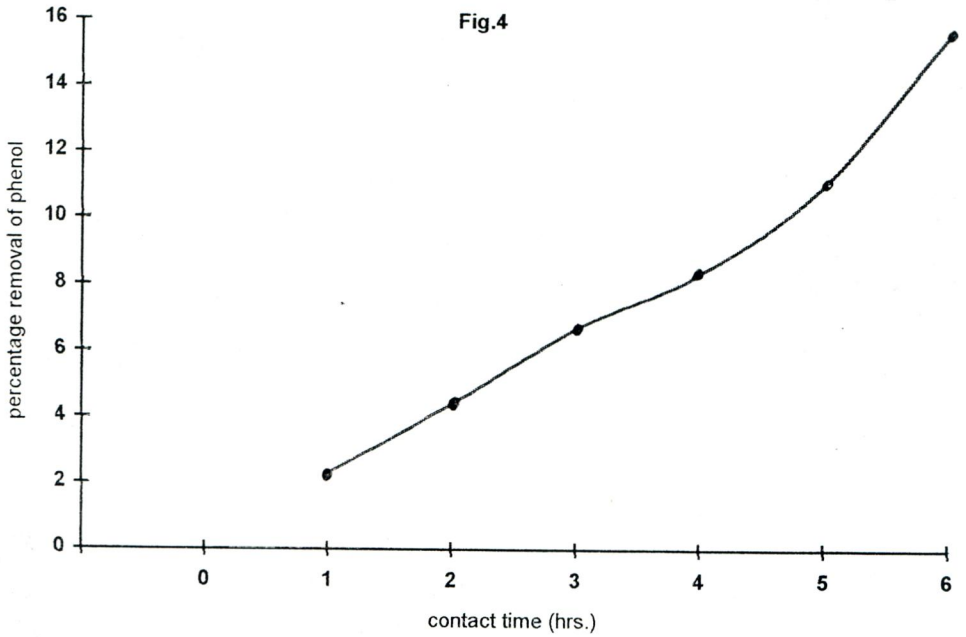



**FIG 4** : Variation of % removal of phenol with contact time.

**CONDITION** : 5 g of flyash shaken with 50 ml . effluent at room temperature.

**pH** : 7.6

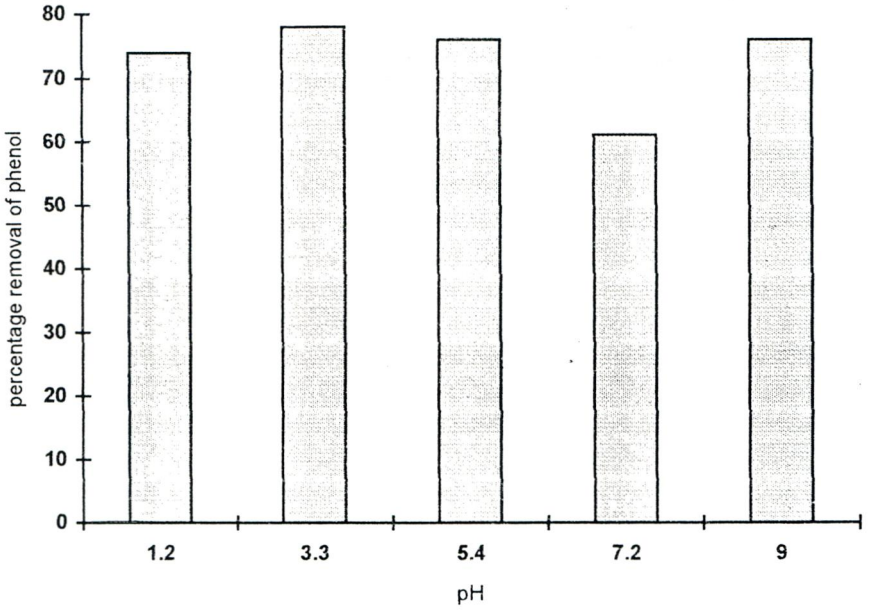



Fig.5

**FIG 5** : Variation of % removal of phenol with pH

**CONDITION** : 200 mg.of activated carbon shaken with 50 ml . effluent at room temperature.

**CONTACT TIME :** 60 minutes.

Fig.6

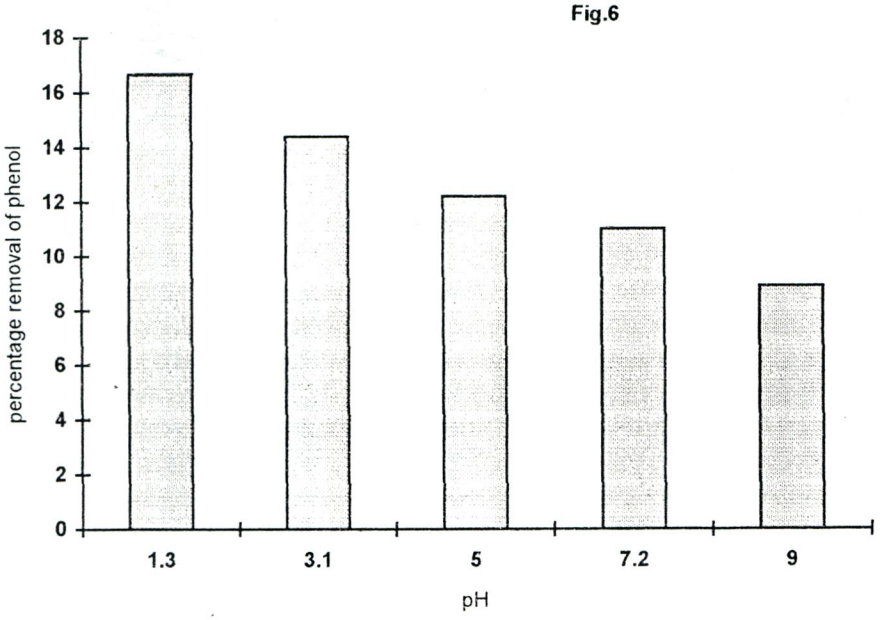
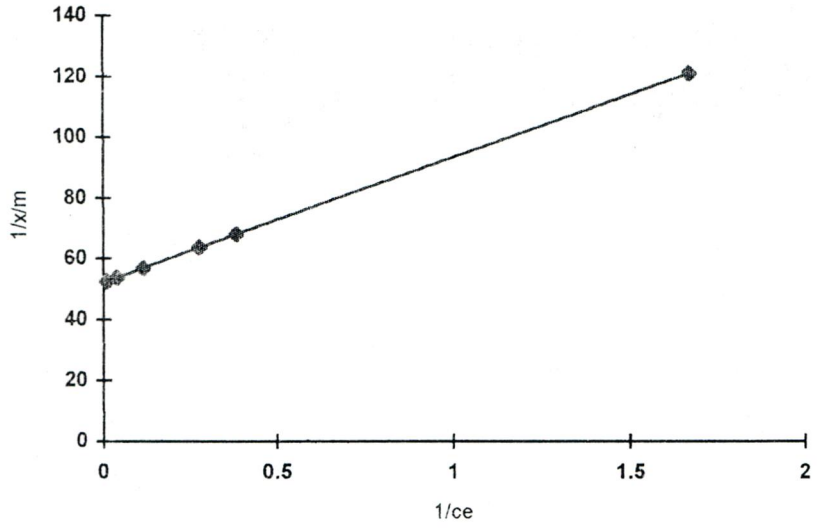



**FIG 6** : Variation of % removal of phenol with pH

**CONDITION** : 5g.of flyash shaken with 50 ml . effluent at room temperature.

**CONTACT TIME :** 3 hrs.




Fi.g7

**FIG 7** : Best fit curve for Langmuir adsorption Isotherm for activated carbon

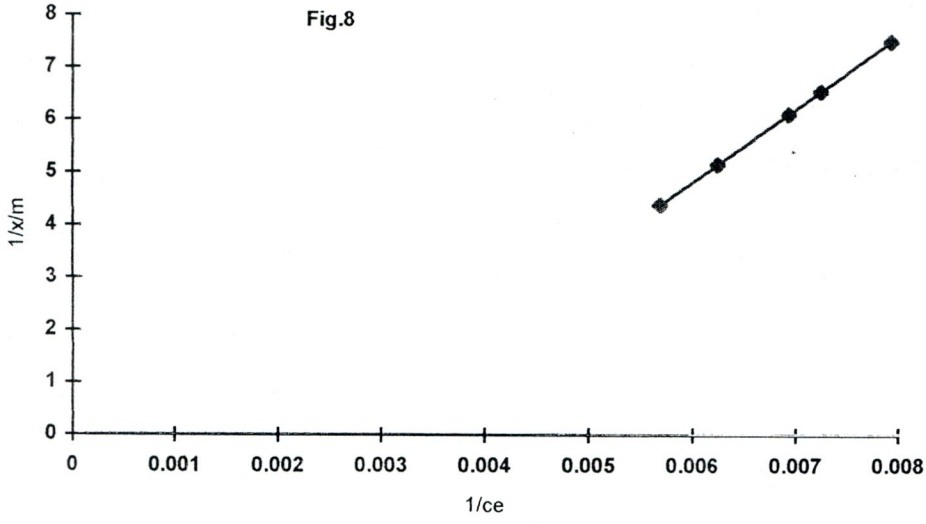



**FIG 8** : Best fit curve for Langmuir adsorption Isotherm for flyash

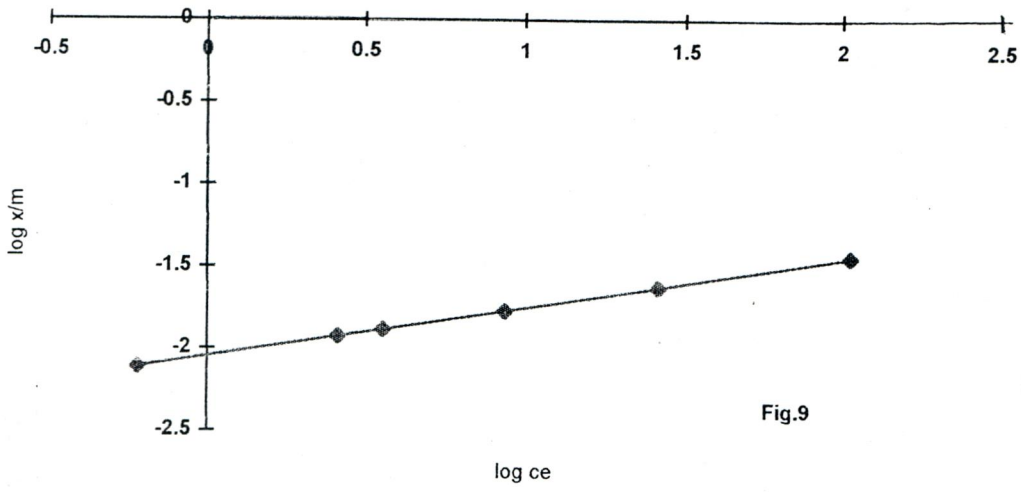



**FIG 9** : Best fit curve for Freundlich adsorption Isotherm for activated carbon

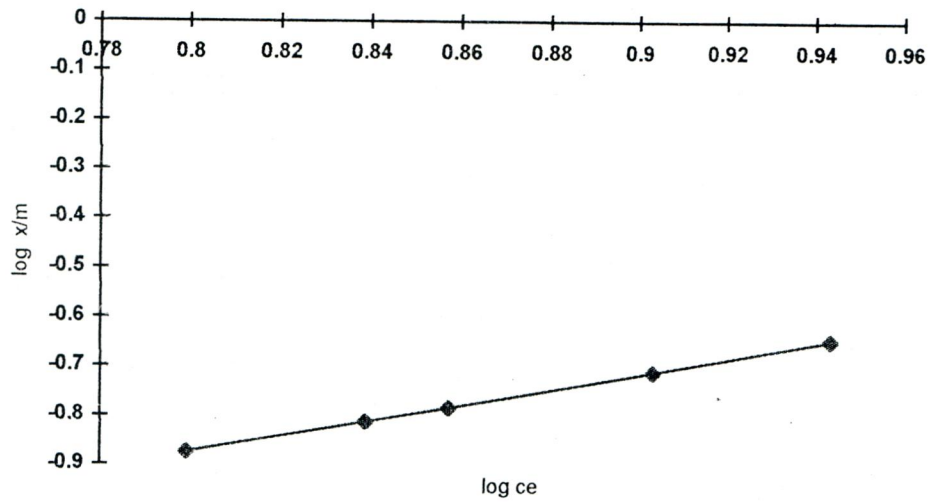



Fig.10

**FIG 10** : Best fit curve for Freundlich adsorption Isotherm for flyash

# Bibliography

# BIBLIOGRAPHY


1. American Water Works Association, Water quality and treatment (New York: McGraw-Hill, 1971).

2. Balasubramaniam M.R.,et. al., Engineering Chemistry, 1992, Chap. 7.

3. Cecil L.K., Ed. Complete Water reuse (New York: American Institute of Chemical Engineering, 1973).

4. Cecil, L.K. Ed. Water reuse symposium series ,78 ,(New York: American Institute of Chemical Engineers, 1967).

5. De.A.K. Environmental Chemistry, Ed.3, pp 195-199, 124-25, 167, (1996).

6. Degremont, Water treatment Handbook, Part II no.507, 407,(1972).

7. Donald. W. Sundstrom, Herbert, E.Klee, Waste Water treatment, Chap. 9. pp 241, (Prentice Hall Inc.),(1979).

8. Handbook of Water resources and pollution control, Edited by Harry Gehm and Jawd Bregman, Van Nostrand Reinhold Company.

9. Health Hazards and Pollution Control in Synthetic liquid fuel conversion Ed. by Perry Nowacki.

   Pollution Tech. Rev. No.68
   Envt. Health Rev. No.2,
   Chem. Tech. Rev. No.165
   Energy Tech Rev.No.57

10. Horsefield D.R. J. Amer Water Assoc. 66, 238,(1974).

11. Ind.J of Envt. Health, 34, No.3, July,(1992).

12. Ind.J. of Envt. Health, 35, No.3 Oct,(1993).

13. Jain and Jain, Engineering Chemistry, Ed-9, Chap.1,(1992).

14. J. American Water Works Assoc, 63:609,(1971).

15. J. Ind Chem Soc 73 No.1 pp 62 Jan.(1996).

16. J. Research and Industry, Vol 4.0(3) 173-266 pp 244-250, Sep(1995).

17. Larry Benefield et.al Process Chem. for waste water treatment, 366-69 (Prentice Hall).

18. Leonard.B.Escritt, Sewage and Sewage treatment, pp 369, International Practice.

19. Manivasagam.N. Chemical Examination of Water Sewage and Industrial effluents, Part V, 224-227,(1985).

20. Marin M.F. Balaguer, M.D. and Rigola. M. Feasibility of activated Carbon production from Biological sludge by chemical activation with $ZnCl_2$ and $H_2SO_4$, Envt Tech.17, 667-672,(1996).

21. Metcalf and Eddy Inc. Waste Water Engineering Collection treatment and disposal, pp 727-730.

22. Otto Folin and Dennis.W,. J.Bio. Chem.22, 305-8 (1915).

23. Philips, W.J., J. Amer. Water Works Assoc. 66:231 ,(1974).

24. Rao, M.N. and Dhatta. K. Waste Water treatment, Ed:2, Chap 18 pp 288, 304-306 ,(1987).

25. Richard. A. Conway, Richard. D. Ross, Activated Carbon Adsorption Handbook of Industrial Waste Disposal, Chap. 5 pp 174.

26. Singh. B.K., N.M. Misra and N.S. Rawal, Sorption Characteristics of phenol on Flyash and Impregnated Flaysh, Ind.J of Envt. Health, 36-37, No.1 - 4 ( 1994 - 1995).

27. Sivanathan Pillai. M. Elements of Statistics, Ed:3, Chap 13.

28. Sven Erik Jorgensen Elsevier, Studies in Environmental Science, Industrial Waste Water Management,(1979).

29. Trivedy R.K. and Goel. P.K., Chemical and Biological Methods for Water pollution studies pp 328-332,(1986).

# Appendices

# APPENDIX 1

## FOLIN CIOCALTEAU METHOD OF ESTIMATION OF PHENOL

### * PRINCIPLE:

The method was based on the reaction between phenols and an oxidising agent phosphomolybdate which resulted in the formation of a blue complex, the intensity of which was measured in a colorimeter.

### * REAGENTS:

Folin Ciocalteau Reagent

20% sodium carbonate

### * PHENOL STOCK SOLUTION:

One gram of distilled phenol was dissolved in distilled water and made upto 1000ml in a volumetric flask.

## * STANDARD PHENOL SOLUTION:

Standard solutions of 20,40, 60, 80, 100, 120 & 140 micrograms per ml.of phenol were prepared from the stock solution. A colourant is produced by reaction with Folin phenol reagent in presence of 20% sodium carbonate and read at 650 nm in a colorimeter. A reference curve is then plotted as absorbance versus concentration of phenol solution.

## * METHOD:

Pipetted out 1 ml of the standard solution, added 1 ml of Folin Ciocalteau reagent and 2 ml 20% $Na_2CO_3$ solution. Heated in a boiling water bath for exactly one minute, cooled and diluted the blue solution to 25 ml with water and measured its absorbance at 570-700m in a Systronics digital colorimeter.If precipitate occurred, filtered through Whatman no.42 filter paper and centrifuged before readings are taken.

The same procedure was carried out for estimation of residual phenol in the synthetically prepared effluent after adsorption studies.

A blank containing all the reagents was used to adjust absorbance to zero.