Some studies on removal of phenol from waste water using low cost adsorbent

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Abstract **-**This paper is aimed to study the potential of **Rice Husk, Activated carbon** in combination with **Amberlite-XAD4** for phenol adsorption from **Bisphenol-A** manufacturing plant waste water. Batch and column adsorption studies were carried out under varying experimental conditions of contact time, phenol concentration in the range of 100-1000 ppm. adsorbent dose and pH respectively. The adsorption of phenol is maximum in the pH range of 7-8. The suitability of the Freundlich and Langmuir adsorption models to the equilibrium data was investigated for phenol-rice husk system. Results showed that the equilibrium data for all the phenol- rice husk system fitted the Freundlich model best within the concentration range studied. However Langmuir model is fitted well for the phenol-activated carbon system for the concentration range 100-1000 ppm. A comparative study showed that rice husk is very effective and low cost adsorbent for phenol removal. The studies showed that the rice husk could be used as a polishing/pretreatment for removal of phenol from water and wastewater in combination with Amberlite-XAD4 and Activated Carbon .

Key words: Bisphenol-A, Phenol, Rice Husk, Amberlite-XAD4, Activated Carbon, Adsorption, Aqueous System, Adsorption model.

A) Introduction

There is growing concern about wide-spread contamination of surface and ground water by various organic compounds due to the rapid development of chemical and petrochemical industries over the past several decades. So, many industrial wastes contain organics, which are difficult, or impossible to remove by conventional biological treatment processes. In the past several decades, extensive research has been conducted to develop innovative and promising adsorbent material for dealing with the treatment problem of contaminated industrial effluents. Phenols and phenolic wastes from chemical and petrochemical industries at low concentration i.e. 100-1000 ppm. are the major threat to the environment and aquatic life as a whole. The ultimate goal of this endeavor is to identify an effective and low cost adsorbent for Removal of Phenol from waste water at low concentration range where other conventional methods are ineffective.

Phenols as a class of organics are similar in structure the more common herbicides and insecticides in that they are resistant to Biodegradation. Phenol is soluble in water. The odor threshold for phenol is 0.04 ppm (U.S.EPA). Their presence in water supplies is noticed as bad taste and odor. In the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste, which is quite pronounced and objectionable. Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health.Stringent US Environmental Protection Agency (EPA) regulation call for lowering phenol content in the wastewater less than 1mg/l.

There are many methods such as oxidation, precipitation, ion exchange, solvent extraction and adsorption for removing phenols and its derivatives from aqueous solution. **Adsorption** is a well-established and powerful technique for treating domestic and industrial effluents. However, in water treatment the most widely used method is adsorption onto the surface of activated carbon. Activated carbons remove many of the impurities occurring in water and wastewater. In spite of these characteristics, because of the high cost and variable performance of carbon regeneration, single use materials are desirable. **(2)** This has led many workers to search for more economical, practical and efficient techniques. Bottom ash, brick-kiln ash, fly ash, peat, soil, wood, saw dust, bagasse and carbonized bark are some new adsorbent used for organic pollutants.**(3)** In the search for new and low cost agricultural wastes material as an adsorbent, Rice husk is an agricultural waste produced as by-product of the rice milling industry to be about more than 500 million tonnes, 70% of which is generated in developing countries. The utilization of this source of biomass would solve both a disposal problem and also access to cheaper material for adsorption in water pollutants control system. Since, the main components of rice husk are carbon and silica (15-22 % SiO_2 in hydrated amorphous

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form like silica gel), it has the potential to be used as an adsorbent. The aim of this study is to explore the possibility of use of rice husk for removing phenol from aqueous solution (**Bisphenol-A manufacturing plant waste water**) in combination with Amberlite-XAD4 and Activated Carbon. The influences of various factors such as initial pH and initial pollutant concentrations, flow rate on the sorption capacity were also studied.

The Freundlich and Langmuir models were used to analyze the adsorption equilibrium.

B) Problem :-

The problem associated with Bisphenol-A manufacturing plant waste water is its low Phenol concentration along with traces of Acetone which affect the performance of E.T.P. plant and bacterial life. (1)

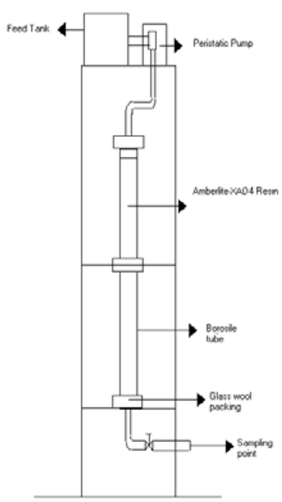
C) Objectives:-

The objectives of the present work are*:*

1) To see the effect of flow rate, concentration of phenol and the presence of other component on adsorption for **phenol-Amberlite-XAD4** system. **(column study)**

2) To find out sorption capacity of rice husk (agricultural waste product) as a low cost adsorbent for **phenol-rice husk** system and **phenol-Activated Carbon system(batch study)**

D) Experimental set up for column study



E) Materials used for column and batch study

PHENOL:

Formula:------------------C_6H_5OH
Molecular weight:-------94.11
Specific gravity:--------- 1.071
Melting point:----------- 42^0C
Boiling point:-------------181.4^0C
Solubility:---------------- 8.2 gm/100 gm of water at 15^0C

Amberlite-XAD4 resin[(5) (6)]:

Specific gravity:---------- 1.025
Form:-----------------------Granular
Colour:---------------------Brown
Microstructure:----------Non-functional, crosslinked.

Sorbent for batch study:

The rice husks used were obtained from Lonere, Raigad district, India. The typical reported composition analysis of rice husk is shown in Table (1). The rice husk

Table 1 [(4)]

Composition	Percentage (%)
Cellulose	32.24
Hemicellulose	21.34
Lignin	21.44
Extraetives	1.82
Water	8.11
Mineral ash	15.05

was crushed and sieved with a 30-mesh siever. Then, the husks were thoroughly washed by distilled water to remove all dirt and were dried at 100^0C till constant weight. The dried husks were stored in desiccator until used.

F) Preparation of Chemicals:

The test solutions were prepared by diluting of stock solution of phenol to the desired concentrations. A stock solution was obtained by dissolving 1.0g of phenol, (obtained from Merck), in cooled distilled water and diluted to 1000 ml. Intermediate phenol solution was obtained by dissolving 100 ml of stock solution of phenol in distilled water and diluted to 1000 ml and finally, standard phenol solution prepared by dissolving 100 ml intermediate phenol solution in distilled water and diluted to 1000 ml. The range in concentrations of phenol prepared from standard solution varied between 100 ppm to 20000ppm. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with diluted and concentrated H_2SO_4 and NaOH solution, respectively. All pH measurements were carried out with a standard pH meter.

G) Analysis of Phenol:

The concentration of residual phenol in the sorption medium was determined by direct Spectrophotometer method. At the end, after the preparation of samples according to the standard methods, the residual phenol concentrations were measured using spectrophotometer equipment (spectrophotometer Thermo-Merck Model). The absorbance of phenol was read at 270 nm.

H) Experimental Procedure for phenol-Amberlite-XAD4 system. (Column study):-

As shown in Fig.(1.0) experimental set-up consists of a 1.0 inch diameter Borosile Glass tube(Burette) of approximately 1.0-m height. For convenience and easy operability it is supported at the center in two parts (using burette stand). At the bottom of the bed strainer is used in the form of glass wool. To avoid air voids as well to keep bottom flow rate constant a liquid head of approximately 1.0 inch is maintained. At the bottom control valve is used.

1) At the top feed tank is kept. The peristaltic pump is used to achieve constant flow rate. Small diameter tubing is used to transport phenol from feed tank to the column. First column was checked for any leaks.
2) Column was filled with water, and then slurry in water was poured up to a 1.0 meter height of column.
3) Solution of appropriate phenol concentration was made.
4) Flow rate was maintained by adjusting the knob of the peristaltic pump.
5) The sample was collected after every 10.0 minutes and checked for phenol concentration by ultraviolet spectrophotometer, which was already calibrated.
6) When less difference in outlet concentration was observed resin was regenerated by acetone.

I) Experimental Procedure for Phenol-Rice Husk system(batch study):-

Sorption studies were conducted in a routine manner by the batch technique. Each phenol solution was placed in 250 ml beakers and a known amount of rice husk(1 to 7g), was added to each beaker. The flasks were agitated on a shaker at a 100 rpm constant shaking rate for 2hr to ensure equilibrium was reached. The supernatant fluid analyzed for the remaining phenol. The studies were performed at a constant temperature of 30ºC to be representative of environmentally relevant condition. Finally the suitability of the Freundlich and Langmuir adsorption model to the equilibrium data were investigated for phenol - sorbent system. All the experiments were carried out in duplicates and the average value were used for further calculations.

J) Experimental Procedure for Phenol-Activated Carbon system (batch study):-

Sorption studies were conducted in a routine manner by the batch technique. Each phenol solution was placed in 250 ml beakers and a known amount of Activated Carbon(0.02 to 0.12 g), was added to each beaker. The flasks were agitated on a shaker at a 100 rpm constant shaking rate for 10 min. to ensure equilibrium was reached. The supernatant fluid analyzed for the remaining phenol. The studies were performed at a constant temperature of 30ºC to be representative of environmentally relevant condition. Effect of phenol concentration on rate of adsorption was also studied for fixed adsorbent concentration of 100mg. and shaking time Finally the suitability of the Freundlich and Langmuir adsorption model to the equilibrium data were investigated for phenol – activated carbon system. All the experiments were carried out in duplicates and the average value were used for further calculations.

K) Results and Discussions:-

For Column study

Experiments for removal of phenol were carried out by using Amberlite-XAD4 resin as an adsorbent in column. The influent concentration of phenol and feed rate was varied and at particular concentration of phenol and effluent concentration was noted down. The same was repeated for different concentration of phenol varying from 100 ppm to 1000 ppm for different feed rate at constant time interval. The feed rate has been changed from 30 ml/min to 80 ml/min. the presence of polar compound like Acetone at different concentration was also studied. From the analysis of the experimental data following points were observed.

Effect of flow rate on percent adsorption:

To study the effect of flow rate on percent adsorption, the percent adsorption of phenol vs. operation time was plotted in figure 2 and 3, It has been observed from the graph that the 90% removal of phenol can be obtained for 30 ml/min to 50 ml/min, whereas same can be obtained for 80 ml/min for 10 minutes duration. This result is obvious and supported by the theory, of course some irregularity has been found for 65 ml/min, which may be due to some experimental error. In general as flow rate increases percent adsorption decreases.

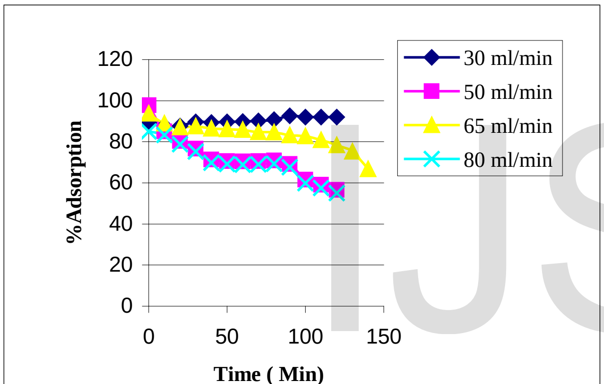


Fig 2 Graph of % Adsorption VS Time for 100 ppm concentration

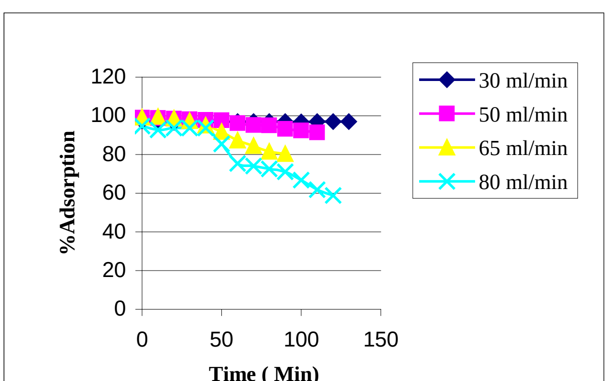


Fig 3 Graph of % Adsorption VS Time for 1000 ppm concentration

Effect of concentration on percent adsorption:

At different flow rates of feed the percent adsorption of phenol was plotted against operation time for different influent concentration. These are shown in figure 4 and 5.The figures showe that at low feed concentration i.e. 100 ppm, 90 percent adsorption was obtained for longer time due to presence of sufficient active sites. For 1000 ppm phenol concentration the percent adsorption obtained was higher as compared to that at low concentration of course for small time span. In general as concentration of phenol in influent stream increases percent adsorption also increases.

Effect of presence of other component on percent adsorption:

To observe the effect of Acetone on percent adsorption of phenol the experimental data obtained was plotted in figure 6. The figure indicate the high influence on increase in percent adsorption. This is happened due to swelling of resin bed. Basically swelling increases the adsorption area of resin, which results in more adsorption of phenol.

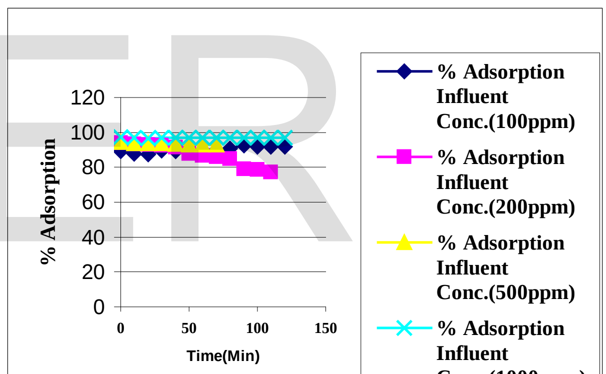


Fig 4 % Adsorption Vs Time for 30 ml/min

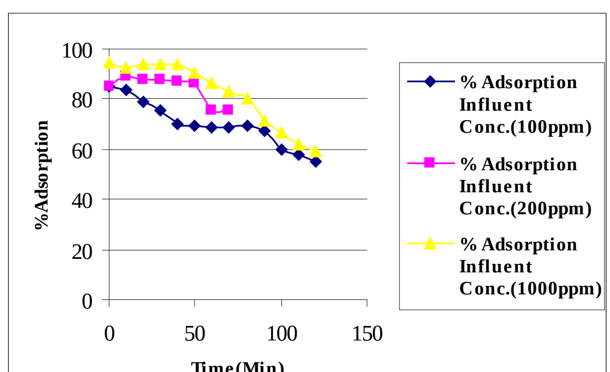


Fig 5 % Adsorption Vs time for 80ml/min

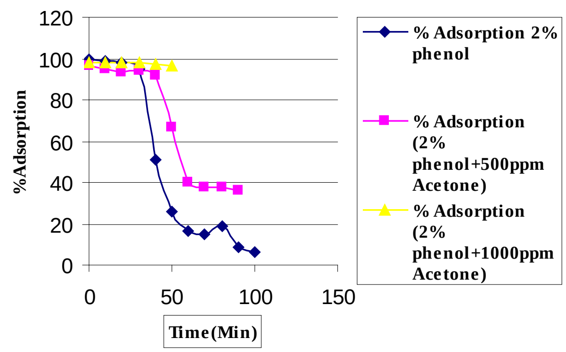


Fig 6 Graph of % Adsorption Vs Time

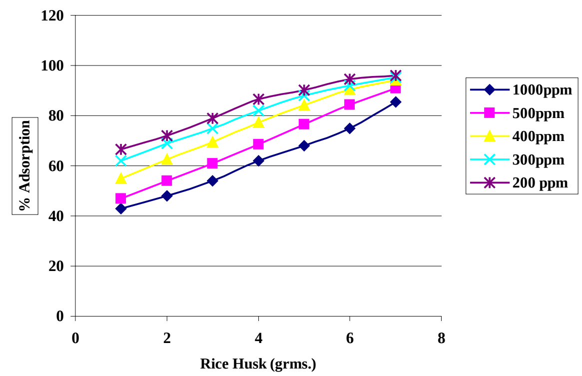


Fig 7 Effect of rice husk on adsorption
(Phenol-Rice Husk System)

For Batch study

Phenol-Rise Husk system

The adsorption of phenol in aqueous solution on rice husk was examined by optimizing various physicochemical parameters such as pH, contact time, and the amount of adsorbent and adsorbate.

Effects of Adsorbent Amount:

The amount of adsorbent on the efficiency of adsorption was also studied. Fig 7shows the removal of phenol by rice husk at the solution pH of 7. Adsorbent dosage was varied from 1g to 7g for rice husk. The results show that for removal of 500 µg/l of phenol in 100 ml of solution, a minimum dosage of 7 grams. of rice husk is requied for 96% removal of phenol. The results also clearly indicate that the removal efficiency increases up to the optimum dosage beyond which the removal efficiency is negligible.

Effect of Contact Time:

The adsorption data for the uptake of phenol versus contact time at 500µg/l initial concentration with 7g rice husk was carried out in pH value of 7. The results Fig 8 show that equilibrium time required for the adsorption of phenol on rice husk was 2hr. These results also indicate that the sorption process can be considered very fast because of the largest amount of phenol attached to the sorbent within the first 120min of adsorption.

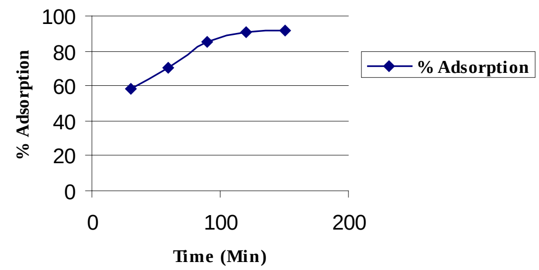


Fig 8 Effect of contact time on Adsorption
(Phenol-Rice Husk System)

Effect of Initial pH:

The adsorption of phenol from aqueous solution is dependent on the pH of the solution, which affects the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate species. The adsorption of phenol by rice husk was studied at various pH values. The

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results are displayed in Fig 9. As was expected, the adsorbed amount decreases with increasing the pH value. This can be attributed to the dependence of phenol ionization on the pH value. Obviously, □ons□□□ ion fraction of phenolate ion) increases as the pH value increased. Accordingly, phenol, which is a weak acid (pKa=10), will be adsorbed to a lesser extent at higher pH values due to the repulsive force prevailing at higher pH values. Also, in the higher pH range phenol forms salts, which readily ionize leaving negative charge on the phenolic group. At the same time the presence of $OH^{(-)}$ions on the adsorbent prevents the uptake of phenolate ions . pH also affects the surface properties of the sorbent, i.e., surface charge of the cells used as sorbent. At very low pH values, the surface of the sorbent would also be surrounded by the hydronium ions, which enhance the phenol interaction with binding site of the sorbent by greater attractive forces, hence its uptake on polar adsorbent is reduced.

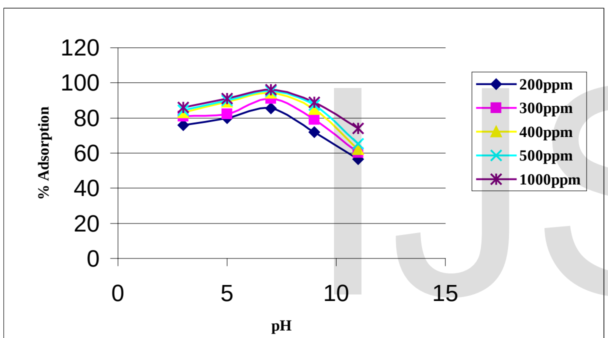


Fig 9 Effect of pH on adsorption
(Phenol-Rice Husk System)

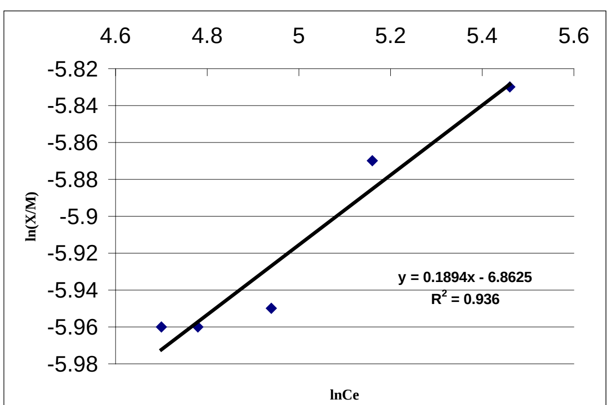
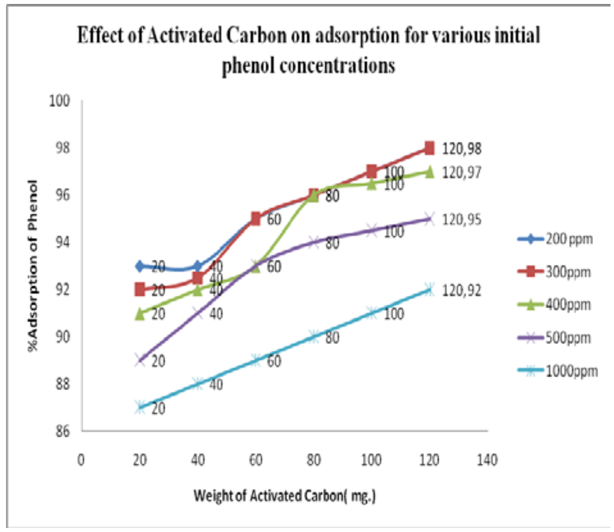


Fig 10 Linearized Freundlich adsorption isotherm
(Phenol-Rice Husk System)

Phenol-Activated Carbon System

Influence of weight of active carbon on phenol adsorption

Test conditions: - Phenol conc. 200-1000 ppm, Shaking time 10 min., Vol. of solution 10 ml



Effect of Initial pH:

The adsorption of phenol from aqueous solution is dependent on the pH of the solution, which affects the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate species. The adsorption of phenol by rice husk was studied at various pH values. The results are displayed in Fig 9. As was expected, the adsorbed amount decreases with increasing the pH value. This can be attributed to the dependence of phenol ionization on the pH value. Obviously, φ_{ions} (ion fraction of phenolate ion) increases as the pH value increased. Accordingly, phenol, which is a weak acid (pKa=10), will be adsorbed to a lesser extent at higher pH values due to the repulsive force prevailing at higher pH values. Also, in the higher pH range phenol forms salts, which readily ionize leaving negative charge on the phenolic group. At the same time the presence of $OH^{(-)}$ions on the adsorbent prevents the uptake of phenolate ions . pH also affects the surface properties of the sorbent, i.e., surface charge of the cells used as sorbent. At very low pH values, the surface of the sorbent would also be surrounded by the hydronium ions, which enhance the phenol interaction with binding site of the sorbent by greater attractive forces, hence its uptake on polar adsorbent is reduced.

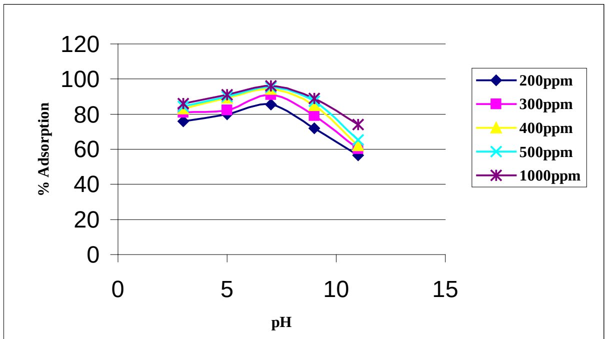


Fig 9 Effect of pH on adsorption
(Phenol-Rice Husk System)

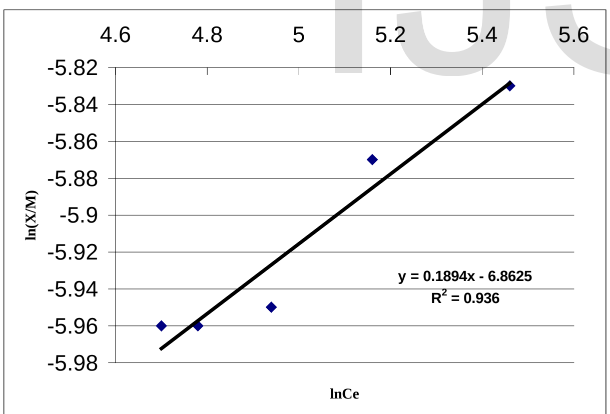
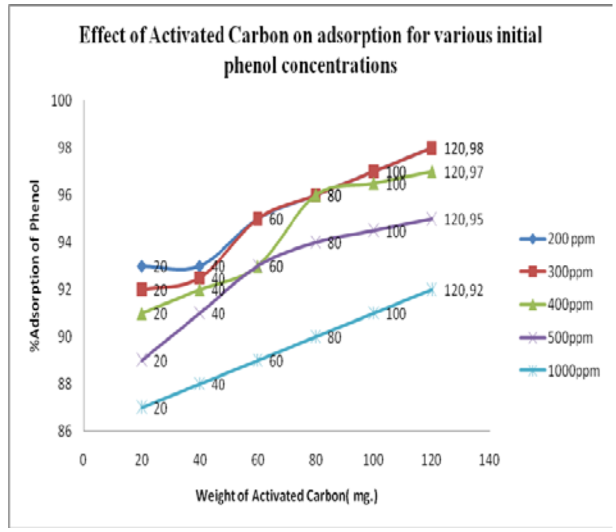


Fig 10 Linearized Freundlich adsorption isotherm
(Phenol-Rice Husk System)

<u>Phenol-Activated Carbon System</u>

Influence of weight of active carbon on phenol adsorption

Test conditions: - Phenol conc. 200-1000 ppm, Shaking time 10 min., Vol. of solution 10 ml

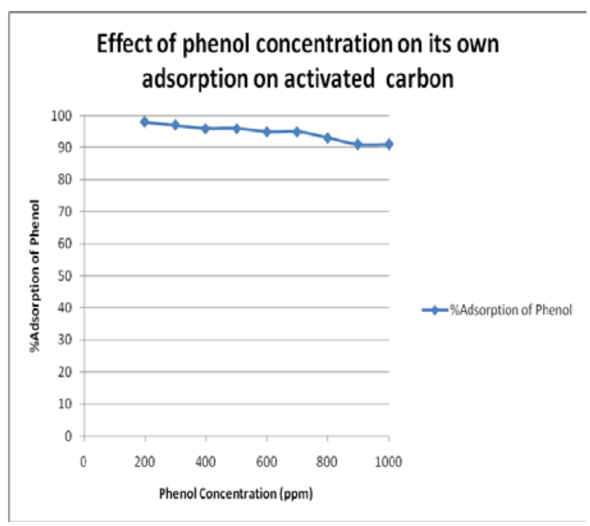


(FIG11)

Results: -The amount of active carbon is employed under the selected condition for shaking time (10 minutes), phenol concentration of 200-1000 ppm, the amount of active carbon was varied from 0.02 to 0.12 g. indicates that the percentage adsorption increases as the amount of active carbon increases. At 0.1 g of active carbon, almost 92% phenol was recovered from solutions. Therefore, 0.1 g of active carbon was used in all subsequent studies

The effect of phenol concentration on its own adsorption

Test conditions: - Phenol conc. 100-1000 ppm, Shaking time 10 min., Vol. of solution 10 ml, carbon dose 100 mg



(FIG12)

The effect of phenol concentration on its own adsorption on active carbon was studied under optimum conditions of a shaking time of 10 minutes and 0.1 g of active carbon. The concentration of phenol was varied from 100 ppm to 1000 ppm. The results shows that the value of percentage adsorption up to 0.3g/l of phenol concentration remained >92%. After that the value of percentage adsorption decreases as the concentration of phenol increases, indicating that less favorable sites became involved in the process with increasing concentration.

The dependence of phenol adsorption on shaking time:-

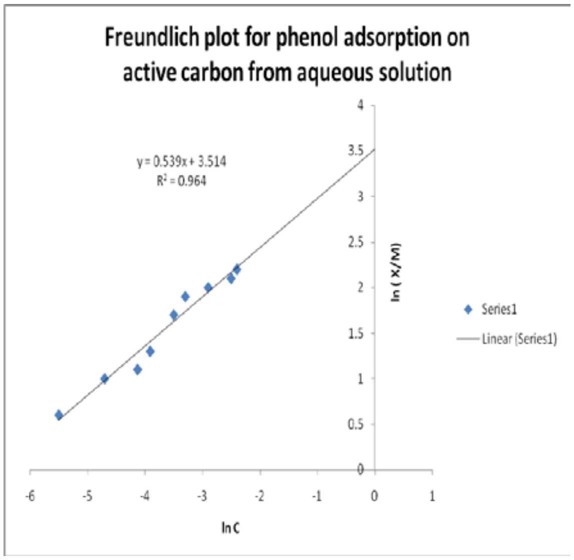
The dependence of phenol adsorption on shaking time was examined in the initial study. The study was performed by shaking 10 ml phenol solution of 0.01 g/l (pH 3.4) with 0.1 g of active carbon for different intervals of time ranging from 2 to 120 minutes. It was observed that the adsorption process is instantaneous and attained equilibrium within five minutes. Therefore, a shaking time of 10 minutes was selected for all further studies. The quick establishment of equilibrium indicates the high adsorption capacity of the active carbon for phenol.

The Freundlich and the Langmuir isotherm equations were used to study data :-

The linearized form of the Freundlich's equation was applied to the adsorption data and is shown in Figure 13,

$$\log X = \log A + 1/n \log C$$

here X is the amount of the phenol adsorbed per gram of the active carbon, C is the concentration of phenol (g/l) left in the solution, i.e. the final concentration, 1/n is the slope showing the variation of adsorption with concentration and A is the intercept, showing the adsorption capacity from solution of unit concentration. This demonstrates the non-validity of the equation over the whole range of concentrations studied.

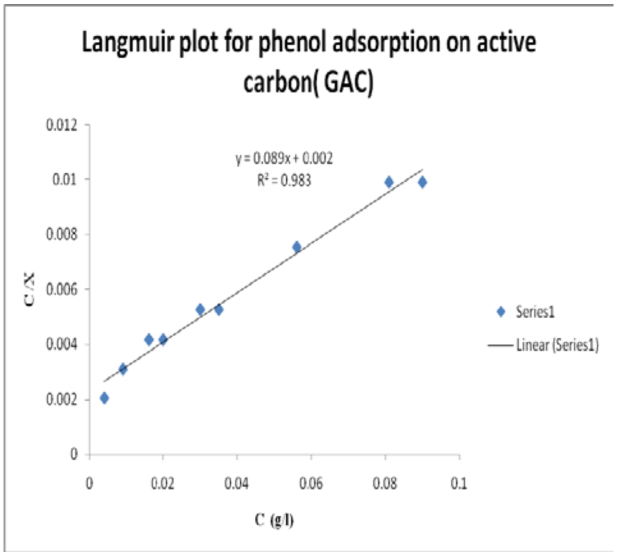


(FIG13)

The Langmuir equation was applied to the data of Figure 13 in the linear form

$$(C/X) = 1/KX + C/X_m,$$

where C and X have already been defined. X_m is the measure of monolayer capacity and K is the constant related to the heat of adsorption. A straight line is obtained by plotting (C/X) versus C (Figure 14), indicating the conformity of the data to the Langmuir equation in the concentration range studied.



(FIG14)

CONCLUSION

Following conclusions can be drawn

- The capacity of the Amberlite – XAD4 resin increases with increase in phenol concentration and also in the presence of other polar component. Phenol can be recovered without any deterioration in its characteristics with a affordable time and cost for reuse. Amberlite – XAD4 resin can be used for waste water treatment of higher phenol concentrations and for recovery

- Rice husk can be used as low-cost, natural and abundant source of adsorbent for the removal of phenol. The adsorptive capacity of rice husk is limited to low concentration and low flow rate. Hence it can be used for a polishing/pretreatment for removal of phenol from water and wastewater. Disposal of rice husk (after use) is easy compare to any other solid waste disposal. After sun drying, Brick manufacturing industry can use Rice Husk or it can be incinerated in waste heat boiler.

- Activated carbon can be used as a effective adsorbent for the phenol adsorption at low concentration (100-1000 ppm) range. The cost of activated carbon is more than Rice husk but less compare to Amberlite-XAD4 resin for same treatment capacity.

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