

Adsorption Studies of Phenol Using Thermally and Chemically Modified Rice Husk as Adsorbents

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ABSTRACT

Most of the Phenols are hazardous substances and some are supposed to have carcinogenic activity. Thus it is necessary to remove Phenolics and other aromatics from the aqueous ecosystem. Traditional processes for the removal of Phenolics compounds are extraction, adsorption on granulated activated carbon, steam distillation, chemical and bacterial techniques. Literature survey show a number of methods like oxidation, ion exchange, reverse osmosis, electrochemical oxidation and adsorption. Phenol removal by process like, adsorption is the best method of choice as it can remove most of phenols in simple and easy way. In recent past; agricultural by-products such as, maize cob, date stone, apricot Stones, rice bran, and bagass pith have been extensively studied and used as adsorbents for the adsorption of hazardous substances from wastewater.

In the present study we tried modified rice husks as potential adsorbents for the removal of Phenol from aqueous system. Batch mode studies were carried out. Isotherm data was generated and fitted in Freundlich and Langmuir equation to explain the phenomenon of adsorption. The adsorption capacities based on Langmuir model (Q_m) of the 3 adsorbents were found to be 0.81 for raw husk (RH), 0.395 for the Grafted (G) and 2.306 mg/g for the Charred (C). The R^2 values were 0.92 for raw husk, 0.97 for grafted and 0.91 for charred husk. Based on Freundlich model the adsorption capacities (K) were 2.94, 2.29 and 1.25mg/g for Raw husk, grafted husk and charred husk. The R^2 values were found to be 0.72, 0.95 and 0.83 for the raw husk, grafted husk and charred husk respectively. Our result showed that modified rice husks could be used as potential adsorbents for Phenol removal from aqueous system.

Keywords: Adsorption, Phenol, rice husk, grafting, isotherm.

1. INTRODUCTION

The primary sources of Phenolics in natural water are, generation during natural decomposition processes or releases in the effluents of brown coal from coking plants, distillery plants, pulp and paper industry, tanning, textiles, plastics, rubber, petroleum and pharmaceutical also contains significant amount of different Phenolics¹. Decay of vegetation also contributes Phenols to aqueous system². Phenols resemble a number of pesticides, which are resistant to biodegradation. Roughly speaking 25% of the pesticides on the world market have a substituted phenol ring³. Phenol is very toxic to humans through oral route; ingestion of one gm of phenol is found to be lethal. The symptoms includes tremors muscle weakness, loss of coordination, paralysis, coma, convulsion, and respiratory problems. Blood changes, kidney and liver damage, cardiac toxicity and low blood pressure have been reported in humans⁴. Activated carbon has been used for the adsorption of phenols & chlorophenols. The kinetics of adsorption of Phenols by granular activated carbon was studied by Zogorski et al⁵. It was observed that 60% to 80% of the ultimate adsorption occurs within the first hour of contact. The adsorption of substituted phenols onto activated carbon produced from olive stones have been studied by Caturla et al⁶. The adsorption process was found to be affected by the porosity of the carbon. A. Kermani et al⁷ studied the removal of Phenol from aqueous solution by using rice husk ash and activated carbon. Batch kinetics and isotherm studies were carried out to evaluate the effects of PH, initial Phenol concentration and adsorbent dose. Maximum adsorption capacity of rice husk ashes prepared at 300, 400 and 500°C and granulated activated carbon was 0.952, 1, 0.989 and 1mg phenol/gm of adsorbent respectively. The study showed that rice husk ash could be used as a new and efficient adsorbent material for the removal of phenol from aqueous solution. Nagda et al⁸ studied the use of leaf refuse of tendu leaf as adsorbent for the removal of Phenol from aqueous system. The adsorption data were modeled by using both Langmuir and Freundlich classical isotherms. The maximum ads capacity of chemically modified leaf refuse was 4 times higher than that of the raw tendu leaf refuse.

Pakistan is an agriculture country. Its major food crops are wheat, maize and rice. Rice is the major food crop and Pakistan is ranked at 12 in the world in producing rice⁹. The rice crop provide white rice which is the favorite food for human consumption but it also produce rice husk as an agriculture residues. The rice husk has got a number of applications. Rice husk can be used to produce mesoporous molecular sieves (e.g., MCM)¹⁰, which are applied as catalysts for various chemical reactions, as a support for drug delivery system and as adsorbent in waste water treatment. Rice husk hulls are an inexpensive source of fiber that is considered a filler ingredient in cheap foods¹¹.

In the present study we used modified rice husk to study its ability to remove phenolics from various aqueous system.

2. RESULT AND DISCUSSION

2.1 Characterization of the adsorbents

2.1.1 Rice husk

Raw rice husk chemical analysis show that it contains 40-50 percent cellulose, 25-30 percent lignin, 15-20 percent ash and 8-15 percent moisture¹².

After burning, most evaporable components are slowly lost and the silicates are left. The typical properties of rice husk are indicated in Table 1. No other plant except paddy husk is able to retain such a huge proportion of silica in it.

2.1.2 Thermal treatment of rice husk

There are two stages in the thermal treatment of rice husk - carbonization and decarbonation. Carbonization is the decomposition of volatile matter in rice husk at temperature greater than 300°C and releases combustible gas and tar. Decarbonation is the combustion of fixed carbon in the rice husk char at higher temperature in the presence of oxygen. The melting temperature of RHA is estimated as 1440°C, that is, the temperature at which silica melts¹³

Table-1: Typical husk analysis [Bronzeoak, 2003]

S. No.	Property	Range
1	Bulk density (kg/m ³)	96 - 160
2	Length of husk (mm)	2.0 - 5.0
3	Hardness (Mohr's scale)	5.0 - 6.0
4	Ash (%)	22.0 - 29.0
5	Carbon (%)	≈ 35.0
6	Hydrogen(%)	4.0 - 5.0
7	Oxygen (%)	31.0 - 37.0
8	Nitrogen (%)	0.23 - 0.32
9	Sulphur (%)	0.04 - 0.08
10	Moisture (%)	8.0 - 9.0

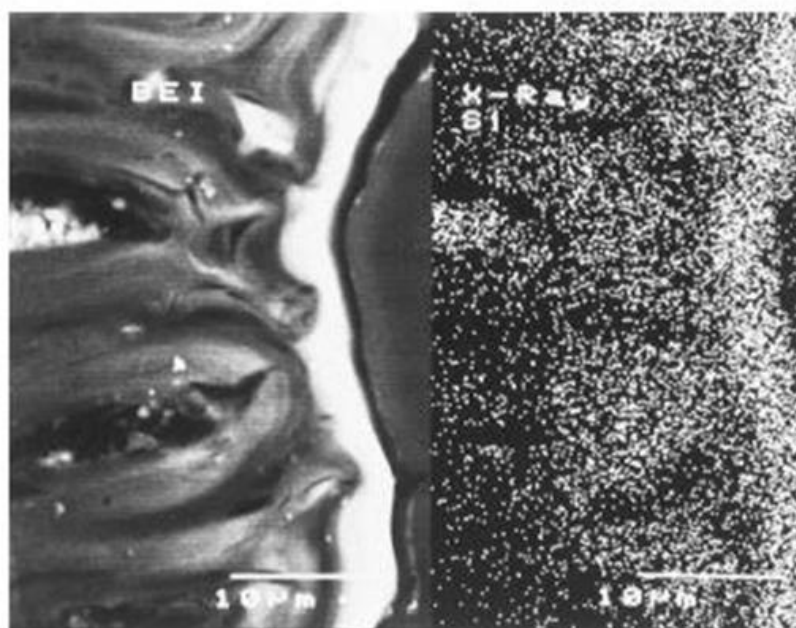


Fig.1: A combined effect of back scattered electron and X-ray images revealing porous husk structure and silica concentration at outer surface¹⁴ [Stroeven et al.,1999]

2.2 FTIR Characterization of the grafted rice husk

The rice husk was hydrolysed with 10% sulphuric acid followed by hydrolysis with 10% sodium hydroxide for 2 hours under reflux(liquor ratio: 1:15 w/v). The purpose of hydrolysis was to remove lignin as far as possible. Grafting was carried out by steeping 2g hydrolysed rice husk in acrylonitril solution for 15 minutes and then added the dissolved hydrogen peroxide (0.3mL) and 0.5g ferric sulphate in glacial acetic acid at 40°C for 2.5hrs (total liquor ration was 1:15, i.e., total quantity of grafting liquor was 100mL). After grafting the sample was filtered washed with distilled water and then dried in air. This dried sample was extracted with distilled water in a soxhlet device for 24hrs to dissolve the formed homopolymer. After extraction, the sample was washed with distilled water and then air dried¹⁵. The functionalized rice husk was characterized by FTIR spectrophotometer shimadzu Prestige-21 as shown in fig 2. The various band specifications of the spectra are given in table no 2.

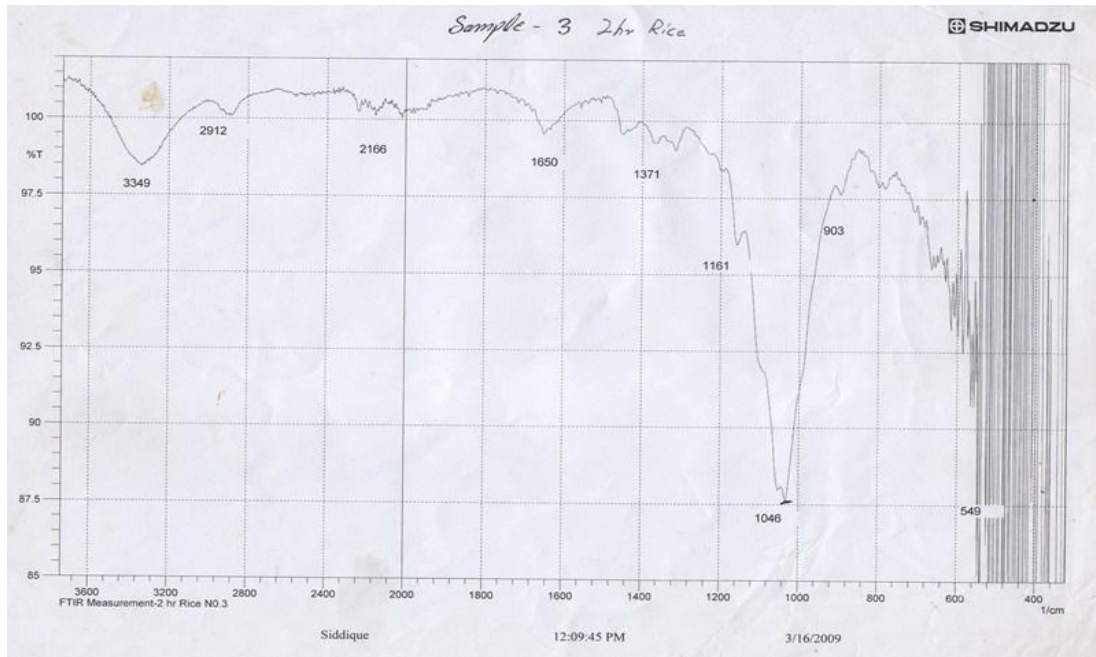


Fig.2: FTIR spectra of rice husk grafted with with acrylonitrile.

Table-2: FTIR band of grafted husk with acrylonitrile

S. No	Frequency in Cm ⁻¹	Functional group
1	3349	-OH stretching
2	2912	C-H stretching(aliphatic)
3	2166	-CN stretching
4	1650	C=C Stretching aliphatic
5	1371	C-H bending aliphatic

2.3 Adsorption studies

The adsorption of phenol on modified husk was carried out by batch technique. Three adsorbents i.e. raw husk (RH), grafted (G) with acrylonitril, & charred (C) were tested to asses their ability to remove phenol from aqueous system by adsorption. The equilibria of the adsorption and the kinetics are two important physico-chemical aspects for the evaluation of the adsorption process as a unit operation. Equilibrium studies give the capacity of the adsorbent and are described by adsorption isotherms. Generally the ratio between the quantity adsorbed and that remaining in the solution at a constant temperature is at equilibrium. There are two types of adsorption isotherms i.e. Langmuir & Freundlich's.

2.4 Langmuir isotherm

The Langmuir model predicts that the uptake of the adsorbate occurs on a homogenous surface by a monolayer adsorption without any interaction between the adsorbate molecules¹⁶. The linear form of Langmuir equation

$$C_e/Q_e = 1/K + a/KC_e$$

Where;

C_e is the equilibrium concentration of adsorbate (mg/L).

Q_e is the amount of the adsorbate adsorbed at equilibrium (mg/g).

The linear plot of C_e/Q_e vs C_e agive a straight line. The various parameter of the Langmuir isotherm are as follow

- a / K = Q_m = slope = adsorption capacity
- 1 / K = intercept of the line
- b = Q_m / K = Energy of adsorption
- a = Q_m

2.5 Freundlich isotherm

The Freundlich isotherm assumes that the uptake of adsorbate occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration¹⁷. The Freundlich isotherm is represented by the linear equation.

$$\ln Q_e = \ln K + 1/n \ln C_e$$

Where,

K and $1/n$ are Freundlich constants,

Q_e is the amount of adsorbate adsorbed at equilibrium and C_e is the equilibrium concentration of the adsorbate in the solution.

A linear plot of $\ln(Q_e)$ vs $\ln(C_e)$ gives a straight line.

The intercept of the line is K (Adsorption capacity),

Slope is $1/n$ (adsorption intensity) and

“n” give the favorability of adsorption ($0 < n < 10$)

These both are called isotherms because it gives a straight line at constant temperature.

2.6 Langmuir isotherm of phenol

The Langmuir adsorption isotherm data of phenol on all the 3 adsorbents are given in table no 4 and fig no 3, 4 and 5. The Langmuir constants for various adsorbents are shown in table no 6. The adsorption capacities (Q_m) of the 3 adsorbents shown in table no 6, shows that it is highest (2.306) for the Charred (C) and lowest (0.395) for the Grafted (G). The highest adsorption capacity of the charred husk (C) show that many sites on the surface of the adsorbent are unoccupied by the adsorbate molecules and most of the adsorbate molecules are still in the solution and are not adsorbed by the adsorbent.

The lowest adsorption capacity of grafted (G) shows the reverse trend and mostly the adsorbate molecules are bonded to the adsorbent surface. The energy of adsorption is found to be maximum for grafted husk (2.13) and minimum for charred husk.

2.7 Adsorption equilibrium data of phenol on the various adsorbents

Table-3: Adsorption equilibrium data of phenol on raw husk, grafted husk and charred husk:

S. No	Conc.	Raw Husk(RH)		Grafted Husk (G)		Charred Husk (C)	
		Ce	Qe	Ce	Qe	Ce	Qe
1	100 μ g	0.81	0.036	0.347	0.060	0.642	0.180
2	200 μ g	1.679	0.070	0.729	0.115	0.292	0.250
3	300 μ g	2.520	0.102	1.466	0.163	1.944	0.280
4	400 μ g	3.256	0.128	2.188	0.217	2.593	0.270
5	500 μ g	4.184	0.162	2.912	0.267	3.163	0.315

Equilibrium concentration in mg/L = Ce

Adsorbed concentration in mg/g = Qe

Table-4: Langmuir isotherm data of phenol on rice husk, grafted husk and charred husk

S. No	Conc.	Rawhusk(RH)		Grafted husk(G)		Charred husk(C)	
		Ce	Ce/Qe	Ce	Ce/Qe	Ce	Ce/Qe
1	100 μ g	0.818	22.4	0.729	12.2	0.642	3.6
2	200 μ g	1.679	24.0	1.466	12.6	0.292	5.2
3	300 μ g	2.52	24.9	2.188	13.2	1.944	7.1
4	400 μ g	3.256	25.3	2.912	13.4	2.593	9.7
5	500 μ g	4.184	25.8	3.665	13.7	3.163	10.6

Equilibrium concentration in mg/L = (Ce)

Adsorbed concentration in mg/g = (Qe)

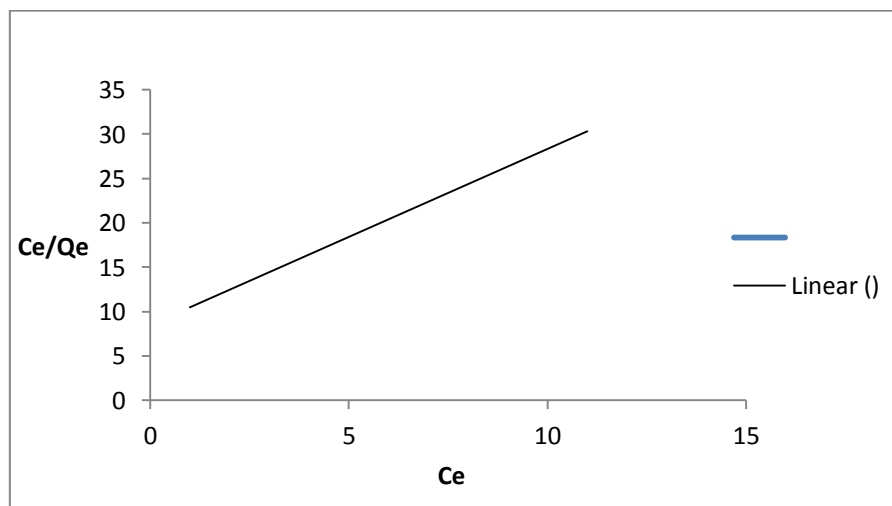


Fig-3: Langmuir adsorption isotherm of phenol on raw rice husk

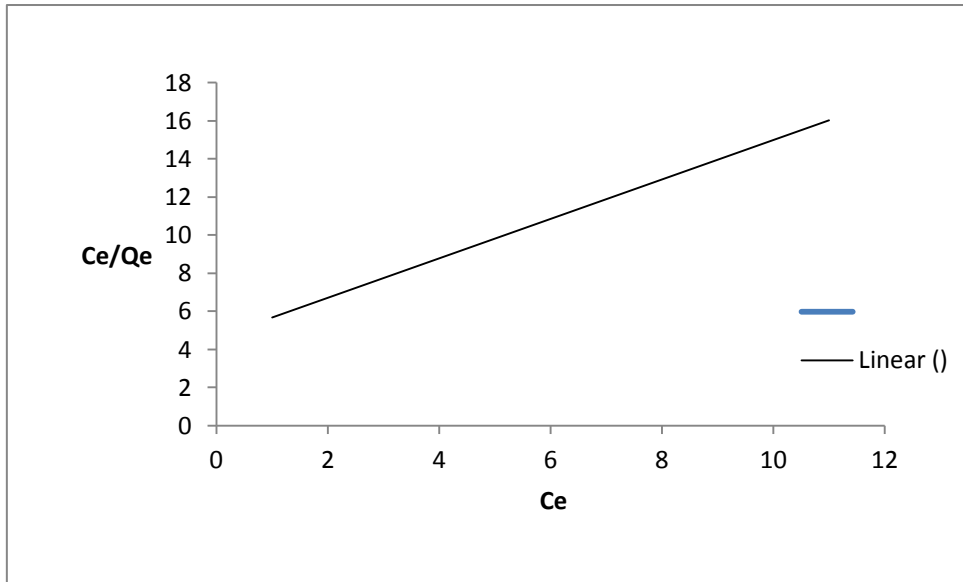


Fig-4: Langmuir adsorption isotherm of phenol on grafted rice husk

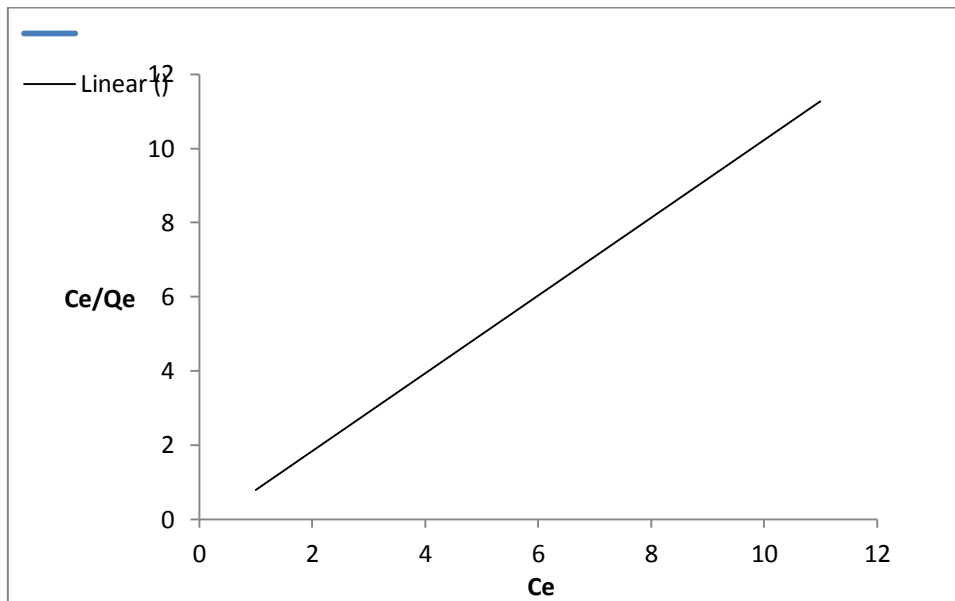


Fig-5: Langmuir adsorption isotherm of phenol on charred rice husk

Table-5: Freundlich isotherm data of phenol on rice husk, grafted husk and charred husk:

S.no	CONC	Ce	Qe	Ce	Qe	Ce	Qe
1	100 µg	-0.20	-3.31	-0.32	-2.81	-0.44	-1.73
2	200 µg	-0.52	-2.66	0.38	-2.16	0.26	-1.40
3	300 µg	0.92	-2.28	0.78	-1.81	0.07	-1.27
4	400 µg	1.18	-2.05	1.07	-1.53	0.95	-1.31
5	500 µg	1.43	-1.82	1.30	-1.32	1.15	-1.12

Equilibrium concentration in mg/L= (Ce)

Adsorbed concentration in mg/g= (Qe)

Raw husk(RH)

Grafted husk(G)

Charred husk(C)

Freundlich isotherm model of Phenol: The Freundlich adsorption isotherm data is given in table no 5. The Freundlich constants are given in table no 7. The adsorption capacities (K) of the various adsorbents show that it is highest (2.94) for raw material (R.M) and lowest (1.25) for Charred (C).The adsorption intensities (1/n) is highest (0.11) for Charred (C) and lowest (0) for raw material (R.M).The n value (which is the measurement of the favorability (0<n<10) of adsorption) ranges from 0 for raw material (R.M) to a maximum of 9.10 for Charred (C).

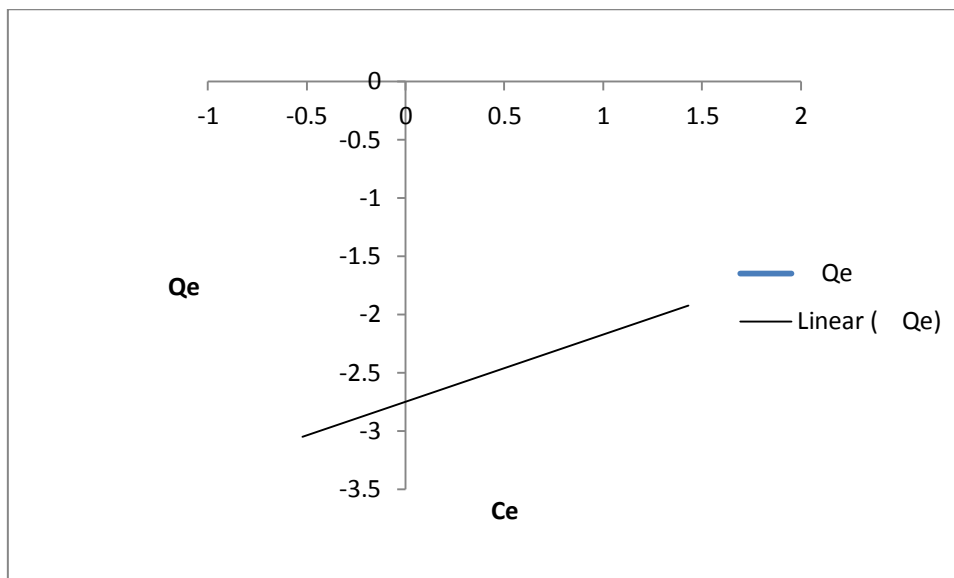


Fig-6: Freundlich adsorption isotherm of phenol on rice husk.

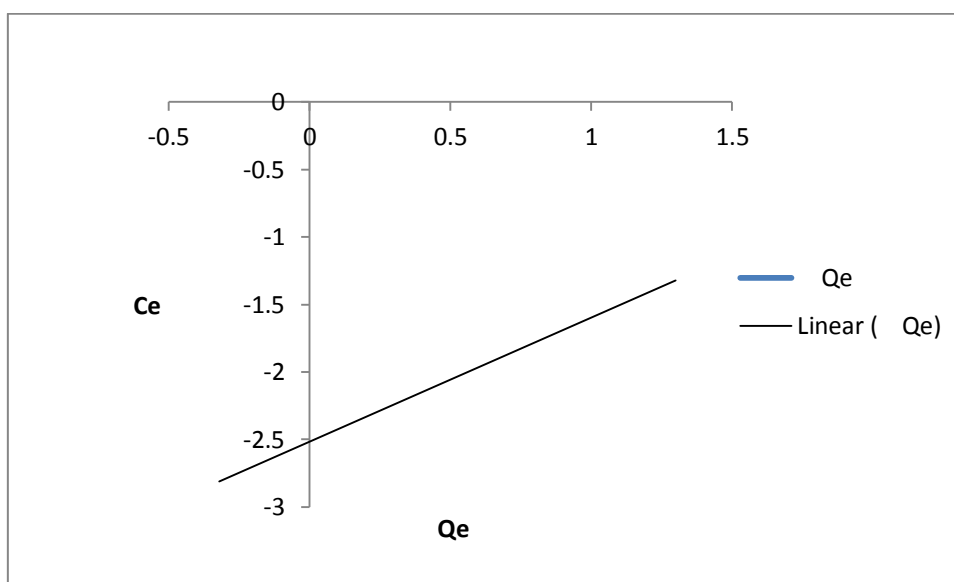


Fig-7: Freundlich adsorption isotherm of phenol on grafted rice husk.

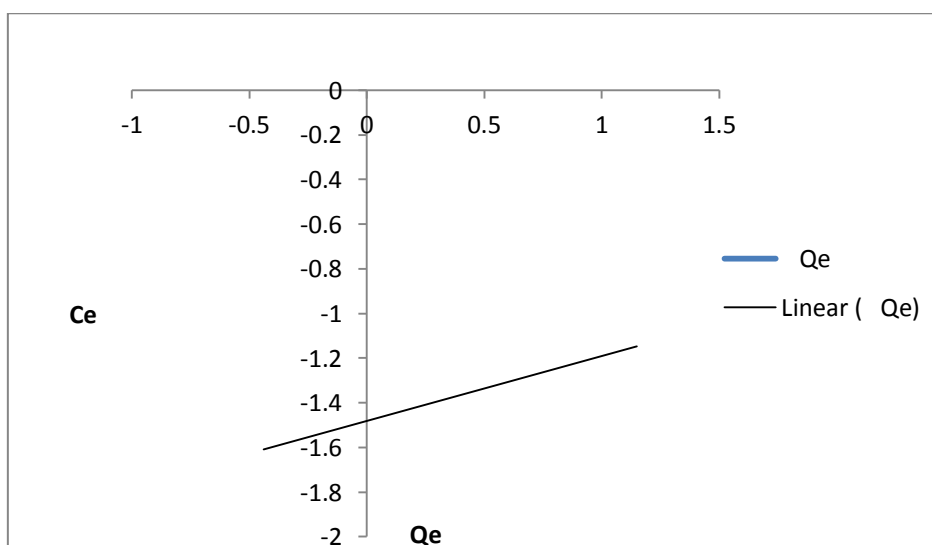


Fig-8: Freundlich adsorption isotherm of phenol on charred rice husk.

The correlation coefficient (R^2) which is measurement of the fitness of the adsorption model is in the range of 0.72 for Raw (R) and a maximum value of 0.95 for Grafted (G). The correlation coefficients of all the adsorbent show that the adsorption isotherm data of phenol on modified rice husk can be well fitted on the Freundlich isotherm equation.

Table-6: Langmuir isotherm constants for Raw husk, grafted husk and charred husk:

S.no	Adsorbent	1/K	K	Qm	R2	A	B
1	Raw husk(RH)	22.1	0.05	0.81	0.92	0.81	0.06
2	Grafted husk(G)	11.8	0.84	0.40	0.97	0.40	2.13
3	Charred husk(CS)	0.00	0.00	2.30	0.91	2.31	0.00

Table-7: Freundlich isotherm constants for Raw husk grafted husk and charred husk:

S.no	Adsorbent	K	1/n	n	R2
1	Raw husk(RH)	2.94	0.00	0.00	0.72
2	Grafted husk(G)	2.29	0.10	9.00	0.95
3	Charred husk(C)	1.25	0.11	9.10	0.83

3. CONCLUSION

The above results show that agriculture residues including modified rice husk can be efficiently and cost effectively used in water treatment technologies for the effective removal of various toxic substances including phenolics.

4. EXPERIMENTAL

4.1 Chemicals

Phenol, 4-amino anti pyrine, Potassium ferricyanide, Ammonium hydroxide (0.5N), distilled water, Chloroform, Potassium mono hydrogen (K₂HPO₄) and potassium di-hydrogen phosphate (KH₂PO₄).

4.2 Materials (Adsorbents)

4.2.1 Rice husk

The husk was obtained from a local rice mill in Swat Pakistan and was used as adsorbents in 3 different forms i.e Raw, Grafted with acrylonitrile and Charred at 250°C for the removal of Phenol from aqueous system.

4.3 Methods

4.3.1 Air drying

The fresh rice husk were subjected to air (in shadowing place) for 36-48 hours, and then weighed after drying.

4.3.2 Oven drying

The air dried rice husk were taken in Petri dish and kept in oven at 100°C for 4hrs to find the moisture content in. The air dried rice husk was used on dry weight bases in the subsequent studies.

4.4 Preparation of adsorbents

4.4.1 Raw husk

The oven dried Husk was considered as raw husk adsorbent and they were directly used for adsorption study.

4.4.2 Grafted husk

The grafting of chemically (acid and base treated) treated rice husk was carried out with acrylonitrile and was used as adsorbent.

4.4.3 Charred husk

Charred husk was obtained by keeping the dried husk in muffle furnace for 3 to 4hrs at 250°C.

4.5 Adsorption of phenol (Batch design study)

Various adsorbents were selected for this study. These includes, raw Husk (R.M), grafted with acrylonitrile husk (G), and charred (C). 5 samples of each adsorbent (0.5gm) was taken in a reagent bottle and various doses of Phenol concentration in the range of 100-500 microgram (μg) of phenol were added. The volume of the mixture was diluted to 50ml. The bottles were agitated on a shaker at 400 rpm for 4hour at room temperature. The samples were centrifuged at 4000rpm for 10 minutes to remove the residual adsorbents. The supernatant was transferred to a volumetric flask. 10ml of Ammonium hydroxide and 10ml of phosphate buffer was added to adjust the pH to 8 by pH meter jenway 3505. The solution was transferred to a separating funnel and 3ml of 4-Aminoantipyrine and 3ml of potassium ferricyanide were added. The mixture was allowed to develop color for 15 minutes. The colored complex was extracted with 25ml of chloroform. The absorbance was recorded for each sample on a UV visible spectrophotometer at 460nm. The amount of residual phenol in the supernatant was determined from the calibration curve¹⁸.

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