



RICE-HUSK AS AN ADSORBENT FOR PHENOL REMOVAL

Pushpa Jha

Department of Chem. Tech., SLIET, Longowal, Sangroor-148106, PUNJAB

ABSTRACT

Phenolic type of substances is objectionable in a disposable waste because of their toxicity to animal and plant life. Concentrations of phenolic waste in chemical and coke oven effluents varies from 1-10,000mg/l. Adsorption/Sorption of phenol by a suitable solid adsorbent/sorbent is a simple and economical process for the purpose. Biomass, particularly agro-residues like rice-husk, bagasse, raw groundnut shell, salseed husk, coconut coir, cotton stalks etc. are available in India abundantly after the harvest. Out of all agro-residues, which are mentioned above, rice-husk seems to be the most appropriate for the study. Rice-husk being the source of carbon can be considered as good material for sorption of phenol from aqueous solutions. An attempt has been made to compare partially pyrolysed rice-husk with commercial grade carbon and propose activated rice-husk char as a sorbent for phenol sorption from effluents. It is found that at residual phenol concentration of 8000mg/l, sorption capacity of activated rice-husk char is 150.0mg. of phenol/g of char. Equilibrium isotherm for sorption of phenol got fitted into Freundlich Isotherm.

KEY WORDS: Activation of Rice-Husk, Commercial Grade Carbon, Equilibrium Isotherm

INTRODUCTION

Concentration of phenolic wastes in effluents of chemical and coke oven effluents are quite high. Chemical, Physical and Biological treatment methods are available for reduction of all levels of initial phenol concentrations. They are successful and in full scale industrial use. It is the objective of any waste treatment plant to reduce the phenolic waste to an acceptable level through a process which is simple to operate and economical.

Characterization of agro-residues is very essential for the proper understanding of their properties and choice of suitable conversion routes. The ones chosen for characterization are the solid residues obtained from rice-husk, bagasse, lantana, raw groundnut shell, sal seed husk, pine needle, coconut coir, bamboo dust, kihar and cotton stalks. Based on this characterization, an agro-residue which provides a suitable product for phenol sorption is selected. Agro-residues like rice-husk [1], bagasse, raw groundnut shell, salseed husk, coconut coir, cotton stalks etc. are available in India abundantly. These are either grossly under utilized or completely unutilized by in-situ burning in the fields as means of disposal. These agro-residues being the source of carbon are considered as good materials for sorption of phenol from coke oven effluents.

Use of activated carbon [4] is reported as well established for removal of trace organics (phenols).

Out of all agro-residues which are mentioned above, rice-husk seems to be the most appropriate for the study. Rice is the major cereal crop of India, covering an area of about 41 million hectares, the largest area under any single crop. According to the available sources, rice-husk is potentially available almost throughout India. In this paper an attempt has been made to propose activated rice-husk char as sorbent for phenol sorption from effluents. It is found that at residual phenol concentration of 8000mg/l, sorption capacity of activated char is 150mg. of phenol/g of char.

Equilibrium isotherm for sorption of phenol got fitted into Freundlich Isotherm.

MATERIALS AND METHODS

Characterization of Agro-Residues

The term characterization [2,3] of agro-residues means to characterize agro-residues in terms of its properties specific to its usage. The suitability of an agro-residue can be based on its physical and chemical properties, availability, cost of procurement, disposal etc. Volatile Matter (V.M.), Fixed Carbon (F.C.) and Ash Contents are the crucial characteristics for the selection of agro-residues as a sorbent for phenol. It is desirable that any agro-residue which is proposed for such a study should have a high F.C. and Ash contents and a low V.M. content.

Agro-Residues mentioned in Table 1 were characterized in terms of Proximate Analysis, Ultimate Analysis and Ash Deformation Temperature. This Characterization is done as per ASTM standards.

Characteristics of Adsorbent/Sorbent

The two central questions to be answered in determining the applicability of sorption are: how much sorbate (material to be removed from solution) can be removed per unit weight of sorbent (material on which sorption will take for this removal to occur) and how long will it take for this removal to occur. Characteristics of Commercial Grade Carbon is shown in Table 2.

Activation of Partially Pyrolysed Rice-Husk

It is perhaps possible to bring the important physical parameters, which are helpful in increasing phenol sorption capacity of Rice-Husk char, close to that of commercial grade carbon. In the previous section it was observed that partially pyrolysed char has very different BET surface area, V.M., F.C., and Ash content than that of Commercial Grade Carbon.

In order to control the above physical parameters and bring them near to that of commercial grade carbon, an attempt is made to activate Rice-Husk Char by the following process:

(i) **Pyrolysis of Rice-Husk:** The Rice-Husk is pyrolysed at 600°C for 90 minutes with 35% yield.

(ii) **Steam Gasification of Rice-Husk:** The char obtained after pyrolysis is gasified at 650°C for 120 minutes.

(iii) **Leaching of Char with HCl:** The char obtained after gasification with steam is leached with 3% Hydrochloric Acid leaching is done at 60°C for 4 hours.

(iv) **Digestion of Char with NaOH:** The leached char is digested with 10% sodium hydroxide in a batch digester. The digestion is done at 70°C for 4 hours.

The solid residue is washed, filtered and dried. The char obtained in this case is called activated carbon. Some of the important physical properties of the activated carbon are given in **Table3**.

Sorption Study on Commercial Grade Carbon/Partially Pyrolysed Rice-Husk/Activated Rice-husk Char

As observed in **Table3**, BET surface area increased by about three hundred times that of partially pyrolysed rice-husk after activation. This indicates that rice-husk char has become much more porous after the activation. An attempt is made to check its sorption capacity for phenol from aqueous solution. Sorption capacity is determined by the sorbent's equilibrium isotherm. For this different quantities of activated char were taken in different conical flasks and mixed with 100.0 ml of aqueous phenol solution in each. All the samples were kept to equilibrate at 37 °C.

RESULTS & DISCUSSION

Characterization of Agro-Residues: As per **Table 1** Rice-Husk is suggested as the best biomass for study of phenol sorption among the materials characterized. It has F.C. and Ash contents of 17.60 % and 16.69 % which are reasonably high. Volatile Matter of Rice-husk is 65.70%. Volatile matter can be brought to very low value by thermal treatment. It is also abundantly available and has otherwise many problems for its efficient and pollution free combustion.

TABLE1. Characterization of Agro-Residues

Agro-Residues	V.M. (%)	F.C. (%)	Ash (%)	Carbon (%)	Ash Deformation Temp.(C)
Bagasse	93.20	4.26	2.54	44.23	1300-1350
Bamboo Dust	71.60	18.48	9.91	42.78	1400
Coconut Coir	69.60	13.20	17.20	47.17	1100-1500
Cotton Stalk	70.89	22.43	6.68	43.64	1320-1380
Kikar	77.01	22.35	0.64	45.89	1300-1350
Lantana	81.67	16.25	2.08	45.01	-----
Pine Needle	72.38	26.12	1.50	79.07	1250-1300
Groundnut Shell	60.80	17.60	5.40	45.30	1180-1200
Rice-Husk	65.70	17.60	16.69	37.03	1430-1500
Sal seed Husk	62.54	28.06	48.12	48.12	1450-1500

Characteristics of Adsorbent/Sorbent: Here Ash, V.M. & F.C. percentages are found by Proximate Analysis. BET surface area analyser gives BET Surface Area. Average particle size is found from Particle Size Analyser. Methylene Blue Test value is found from standard method

which indicates sorption capacity of the sorbent. Some very crucial physical properties of Commercial Grade Carbon which is used as industrial adsorbent is given in Table2

TABLE2. Some Physical Properties of Commercial Grade Carbon

Physical properties	Quantities
Ash	1.46%
V.M.	7.28%
F.C.	91.26%
B.E.T. Surface Area	1055.4m ² /g
Methyl Blue Test Value	210mg/g
Average Particle Size	27.2microns

Equilibrium studies [6,7] on Commercial Grade Carbon is done to have an understanding of the effect of all above mentioned physical properties on the process of sorption with 0.95% phenol solution(0.95% conc. was chosen as coke-oven effluent has approx. this conc.) as sorbate. This is shown in **Fig.1**

Comparison of Sorption Capacity of Partially Pyrolysed Rice-Husk with Commercial Grade Carbon

To compare the sorption capacity of rice-husk char very crucial physical properties (same as that of commercial Grade Carbon as shown in Table 2) is considered for comparison.

After the comparison one finds that BET surface area of Commercial Grade Carbon is approximately thousand times compared to that of Pyrolysed Char. Methylene Blue

test value is 210mg/g for Commercial Grade Carbon where as the same property is 0.0mg/g for Partially Pyrolysed Rice-Husk. Percentages of Ash, V.M. &F.C. are 24.84, 48.96 & 42.26 respectively for Partially Pyrolysed Rice-Husk where as same properties for commercial grade carbon is 1.46, 7.28 and 91.26 respectively. This indicates that any ideal sorbent for sorption of phenol of 0.95% concentration should have very high percentage of F.C. and low percentage of Ash and V.M.

Equilibrium studies on Partially Pyrolysed Rice-Husk [5] is done to have an understanding of the effect of all above

mentioned physical properties on the process of sorption with 0.95% phenol solution as sorbate. This is shown in **Fig.1** From this figure one can compare and observe that sorption capacity of Commercial Grade Carbon is very high throughout the range as shown in **Fig.1**. One can observe that it is 8.42 times that of partially pyrolysed char at residual concentration of 6330mg/l.

All above observations suggest that Partially Pyrolysed Rice-Husk needs to get activated thermally & chemically in order to make it a better sorbent.

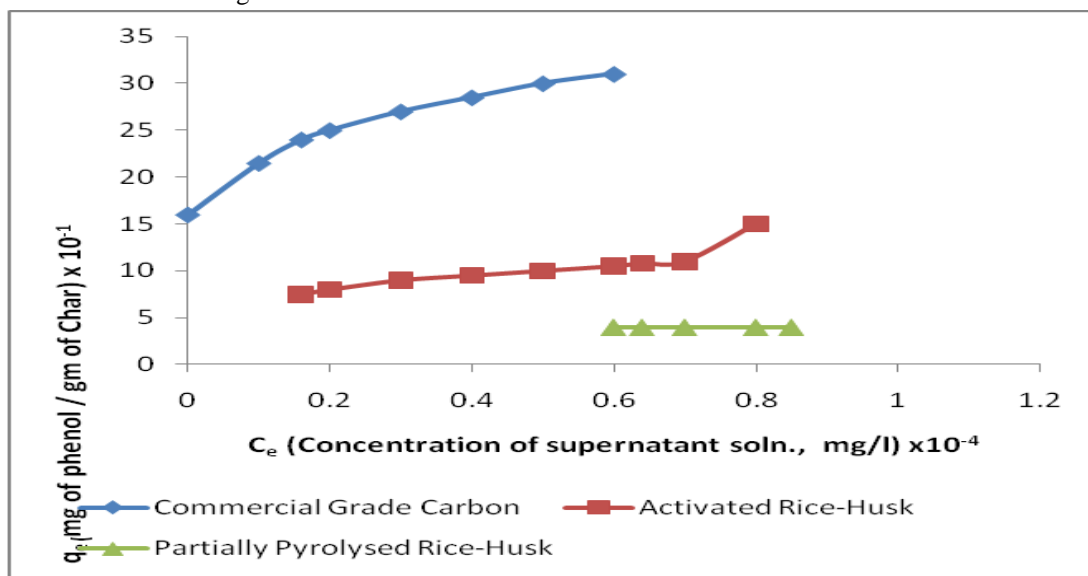


FIGURE 1. Comparison of Equilibrium Isotherms of Different Sorbents (Temp. = 37°C)

Sorption Study on Activated Rice-husk Char: After activation of Partially Pyrolysed Rice-Husk Char as explained in 2.3, its physical properties were studied as shown in **Table 3**. All characteristics of this activated char from adsorbent point of view have clearly improved. This activated char is studied for phenol sorption by studying its equilibrium isotherm at same conditions as that of commercial grade carbon and partially pyrolysed rice-husk and it is found that sorption capacity is improved four times that of partially pyrolysed char of rice-husk which is very clearly shown in **Fig.1**. This figure shows graphical representation of the sorption isotherm which represents relationship between the equilibrium distribution of sorption with concentration of sorbate in the solution at 37°C. As usual the amount of phenol sorbed per unit weight of activated rice-husk char (q_e) increases with increasing concentration of supernatant solution (C_e). It is seen from **Fig1** that at residual phenol concentration (C_e) of 80.00×10^2 mg/l, sorption capacity of activated char is 150.0 mg. of phenol/g of char. At $C_e = 46.00 \times 10^2$ mg/l, sorption capacity of activated char is 98.0mg of phenol/g of char. At $C_e = 17.00 \times 10^2$ mg/l, sorption capacity of activated char is 78.0mg of phenol/g of char. The experimental data got fitted into Freundlich Equilibrium isotherm with the equation

$$q_e = 5.64 C_e^{1/2.86} \quad \dots (1)$$

Fitting of data in Freundlich isotherm [8] indicates that sorbent surface is probably heterogeneously distributed with sorption sites.

TABLE3. Some Physical Properties of Activated Rice-Husk Char

Physical Properties	Quantities
Ash	6.22%
V.M.	10.59%
F.C.	83.19%
BET Surface Area	290.3m ² /g
Methyl Blue Test Value	52.5mg/g
Average Particle Size	20.39microns

CONCLUSIONS

1. Pyrolysed rice-husk sorption capacity for phenol can be brought near to that of Commercial Grade Carbon properties by activating it thermally and chemically.
2. Equilibrium isotherm for sorption of phenol got fitted into Freundlich Isotherm indicating that sorbent surface is probably heterogeneously distributed with sorption sites.

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