POTENTIAL OF PHENOL REMOVAL BY LOW COST ADSORBENT IN A BATCH REACTOR

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ABSTRACT

Phenolic compounds have been found to be the primary pollutants in wastewaters. The petroleum industry has served as a major contributor to the pool. In this study, the removal of *Phenol* by adsorption using *Rice Husk* (RH) as the primary adsorbent was investigated by experimentation in a batch reactor. Approximately 120 million tonnes of RH is being produced every year as a by-product of rice paddy cultivation and their disposal is still regarded as a colossal task. The reaction parameters such as pH, residence time, and temperature were analysed for their effects on the removal of phenol by adsorption using RH in a batch reactor. A *Mathematical Model* was formulated by grouping parameter affecting the adsorption and was found consistent with earlier models put forth for different adsorbents. The adsorption tendency was found to decrease with an increase in pH of the solution. There was an observable increase in the removal efficiency of phenol with an increase in the residence time. The phenol adsorption data was found to follow the Langmuir Isotherm in the range studied.

Key words: adsorption, phenol removal, rice husk, mathematical model

I. INTRODUCTION

Phenols are toxic to human beings, fish and to several other phytoplanktons. Ingestion of 1 g phenol is reported to be lethal for humans. Moreover, there exists an increasing concern that consumption of water containing high phenolic compounds may lead to cancer. Due to these adverse health effects of phenols, the World Health Organization [1] has set a limit level of 1 mg/ l to regulate the phenol concentration in drinking waters. Several methods with different removal performance and cost levels are available for the treatment of phenolic wastewaters. Those commonly used are adsorption, chemical oxidation and biological treatment processes [2]. The cost effectiveness of adsorption techniques are almost unparalleled by any other. Large scale use of the biodegradation practices are still only on paper. Chemical oxidation, on the other hand, holds less promise on the economic front. Virtually all development in the field has been in the area of adsorption, while biodegradation has been picking up [3]. Activated carbons are the most common adsorbent [4], and they are made from different plants, animal residues and bituminous coal [5]. Depending on the composition of industrial wastewaters, one type of carbon may be superior to another [6].The production of activated carbons from agricultural by-products serves a double purpose. First, it converts unwanted, surplus agricultural waste to useful, value-added adsorbents [7, 2]. Second activated carbons are increasingly used in water for removing organic chemicals and metals of environmental are economic concern.

II. PREPARATION OF SORBENT

The rice husks were obtained from South Tamil nadu in Southern India, a source variety-Co36. The rice husks were washed twice with distilled water and sorted according to their sizes after drying at about 115°C in a hot air oven. About 95% of the adsorbent particles passed through BS-44 sieves and were retained on BS-60 sieves. The RH was stored in water-proof containers for further use.

III. MATERIALS AND METHODS

The prepared and stored RH sorbent-particles were retrieved and batch experiments were carried out by taking different sorbate concentrations in the range of 10 mg/l to 70 mg/l. The solutions were prepared from the standard stock solution. Care was taken to keep this stock solution away from sunlight and air, as phenol degrades when in contact with both. It was necessary that every alternate day the stock solution be prepared to account for any negligence in the above procedure. 100 ml of the solutions of desired sorbate concentrations were taken in a series of 250 ml

Ermanlayer conical flasks and known amount of rice husk (RH. 0.5 g) were added to each flask. The flasks were agitated on a shaker at a 120 rpm for 3 hours to ensure equilibrium was reached. The experimentation was carried out for estimation of the characteristics of the removal of phenol by the adsorption process, through monitoring of four parameters like pH of solution, temperature, initial concentration of adsorbent and residence time. The initial concentration of 50 mg/l was maintained for studying the effect of pH, temperature and residence time on phenol adsorption.Every reading was taken after sampling in test-tubes that were covered and placed in dark containers. All experimental conditions were repeated twice for better validity.

IV. ESTIMATION OF PHENOL CONCENTRATION

The concentration of residual phenol in the sorption medium was measured by a *uv-spectrophotometer* (Thermo-Spectronic, model: Genesys-10 uv) at 500 nm by using 4-antiaminopyrine method (7). The samples provided contained only phenol and water in solution and hence a blank solution of water was used to set the scales for the uv-absorbance values. The spectral readings were taken for samples of known concentrations of phenol and kept as standard.

V. RESULTS AND DISCUSSION

The adsorption of phenol by rice husk was examined by optimizing various physicochemical parameters such like pH, contact time, temperature and initial concentration of phenol in sorbate solution.

Effect of pH on phenol removal

One of the major factors that affect the adsorption characteristic was observed to be the initial pH of the solution. Hence it becomes necessary to observe the characteristic changes it produces in the adsorption behaviour of the system under consideration. The pH of the solution was adjusted using 0.1 N HCl solution and 0.1 N H_2SO_4 solution so that a desired value was achieved. The adsorption of phenol from aqueous solution was found to be highly dependent on the pH of the solution, as shown figure 1. The results suggested a maximum in the adsorption capacity of 14.8% at pH 8. The pH is known to affect the surface charge of the adsorbent, degree of ionization and specification of the adsorbate species. The percentage adsorption increased pH 8 and the decreased there after.

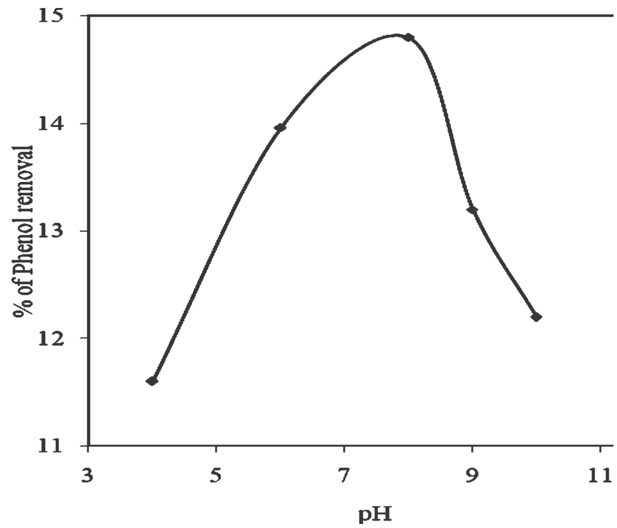

Fig. 1 Effect of pH on Phenol removal

Effect of residence time in phenol removal

The adsorption data for the adsorption of phenol against varying residence times, at 50 mg/l of phenol concentration with 0.5 g rice husk, was taken by carrying out sorption studies at a pH value of 8.0. The results from kinetic analysis show that equilibrium time required for the adsorption of phenol on rice husk almost exceeds 3hr. The result also indicates that the sorption process can be considered very fast because of the largest amount of phenol attached to the sorbent within the first 120 min of adsorption. The kinetics of phenol adsorption on rice husk follows the first-order

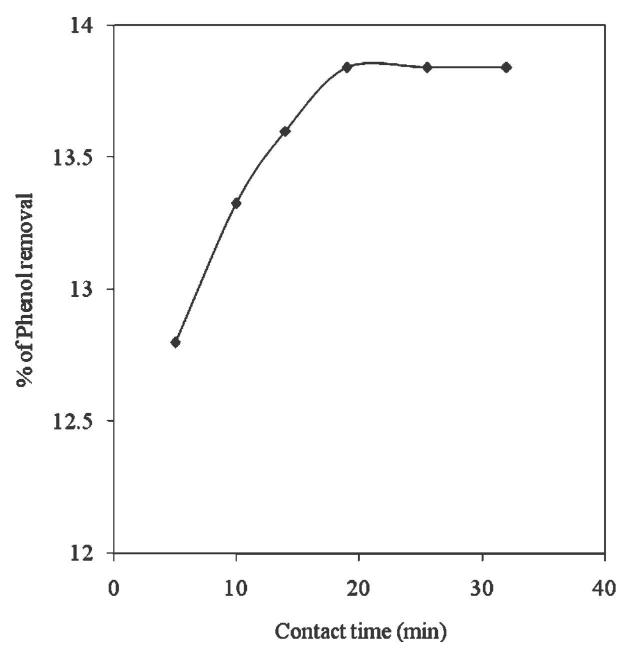

Fig. 2 Effect of contact time on Phenol removal

rate expression. Due to lack of stable power and other time considerations the kinetic studies were dropped to 3 hours. The analysis of the effect of the residence time on the adsorption characteristics yielded that there was an observable increase in the amount of phenol adsorbed per unit mass of adsorbent with a rise in contact time as shown in figure-2 for first 20 minutes and remained constant.

Effect of temperature on phenol removal

Adsorption experiments were carried out at three different temperatures 30°C, 40°C and 50°C at pH 8.0. It can be observed from figure-3 that the percentage adsorption decreases for the feed concentration of 50 mg/l when the temperature was raised.

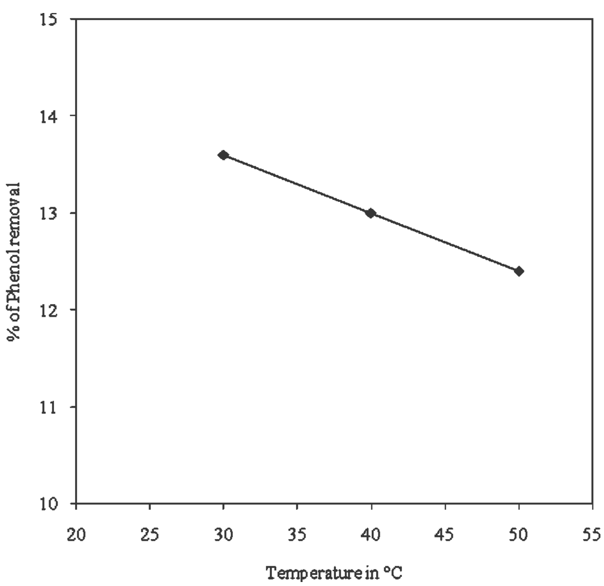

Fig. 3 Effect of Temperature on phenol degradation

Effect of Initial concentration on phenol removal

It was observed that the phenol in effluent followed a linear trend compared to the initial phenol in the feed solution. Figure-4 shows the removal of phenol by rice husk at the solution pH of 8 at 30$C. The adsorbent concentration used was 0.5 g, even though a different optimum exists for every sorbate concentration used. It is evident that for the quantitative removal of different values of phenol in 100 ml, a high dosage of rice husk is required. As seen from results, with increasing phenol concentration, the adsorption yields of phenol showed the opposite trend. Research in the area has shown that the sorption capacities of the sorbents increased with increasing phenol concentration [8]. But when initial phenol concentration

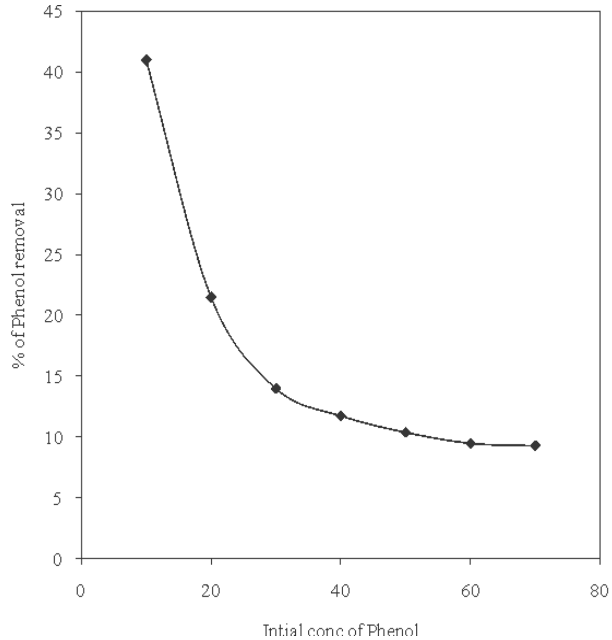

Fig. 4 Effect of intial concentration in phenol removal

was increase from 10 mg/l to 70 mg/l on 0.5g of rice husk the percentage adsorption of phenol decreases.

But the loading capacity must increase due to increasing mass transfer driving force and therefore, eventually, the rates at which phenol molecules pass from the bulk solution to the particle surface will increase, which would result in higher phenol adsorption [3]. The decrease in efficiency has been found to have a more or less exponential decrease. This supports the theory that increasing sorbate concentrations in solution leads to blockage of active sites or pores on the surface of the adsorbent particles due to mass interaction of the particles.

VI. MODELLING OF PHENOL ADSORPTION

Several models have been published in the literature to describe experimental data in the form of adsorption isotherms. The adsorption isotherm depicts the equilibrium relationship between the concentrations of component (phenol) in the two phases (effluent and adsorbent) at a given temperature. Analysis of the isotherms is important in order to develop an equation that accurately represents the results and which could be used for design purposes. In this work, two models were used to describe the relationship between the amount of phenol adsorbed and its final concentration.

The linear form of the Freundlich isotherm model is given by the relation:

$$\log q_e = \log k + n \log c_e \qquad \text{I}$$

Where, q_e-amount of phenol adsorbed per unit mass of adsorbent (mg/g)

c_e-final or equilibrium concentration of the adsorbate (mg/l);

k, *n*-Freundlich's constants related to adsorption capacity and adsorption intensity of the sorbent. The values of '*k*' and '*n*' was obtained from the linear plot of log q_e vs. log c_e, from the experimental data. This was done and the resultant curve and the data are displayed in figure- 5.

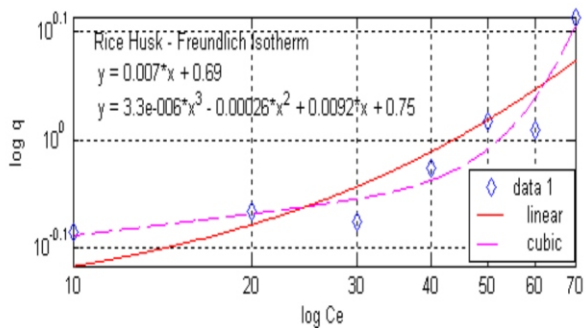

Fig. 5 Freundlich Constants

Lower conformance levels were achieved partially because of the normal conditions utilized. There seems to be lesser adherence to the Freundlich adsorption isotherm .The basic assumption of the Langmuir isotherm process is the formation of a monolayer of adsorbate on the outer surface of the adsorbent and that no further adsorption takes place. The linear form of the Langmuir isotherm model can be represented by the following relationship

$$\frac{1}{q} = \frac{1}{b\, q_m c_e} + \frac{1}{q_m} \qquad \text{II}$$

where,

q-amount of phenol adsorbed per unit weight of adsorbent (mg/g);

c_e-equilibrium concentration of the adsorbate (mg/l)

q_m, *b*-Langmuir constants denoting the significance of adsorption capacity (mg/g) and energy of adsorption (l/mg) respectively. The values of 'q_m' and '*b*' can be obtained from the plot of 1/q vs1/c_e. The results were tabulated and are furnished in table-1.

Table 1

Isotherm Constants			
Freundlich Constants		**Langmuir constants**	
k (mg/g)	**N**	**q_m (mg/g)**	**b (l/mg)**
0.6900	0.0070	1.2346	0.1209

An observation of the isotherm parameters shows a not so favourable condition for adsorption. This is because of the use of normal parameters as discussed above, in contrast to the optimum parameters that could be used. The rice husk used for adsorption clearly exhibits a more uniform surface characteristic as is evident from its nearer depiction of the Langmuir isotherm model at the process conditions Figure-5. expresses the Langmuir isotherm along with the data analysed.

VII. CONCLUSION

In this study, the ability of rice husk to bind phenol was investigated as a function of pH, residence time, temperature and initial phenol concentration. The rice husk adsorption capacity was strongly dependent on pH temperature and initial concentration the phenol in solution. The sorption capacity decreased with an increase in the pH, temperature and initial phenol concentration. The models proposed, agree with most of the existing models. The Langmuir isotherm model better expresses the removal of phenol by the rice husk. This was found by studying the normality distribution of the residuals of the Langmuir and Freundlich Isotherms. The adsorption characteristics of rice husk provide ample justification for its use on the industrial scale. The use of rice husk to the more refined form-activated carbon can save a lot in terms of production and environmental safety costs.

REFERENCES

[1] WHO (1994), Environmental Health Criteria 161: Phenols Standards., International Programme on Chemical Safety (IPCS), INCHEM, World Health Organisation, Geneva

[2] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi (2003), *Utilisation of*

various agricultural wastes foractivated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions., Bioresource Technology, Vol-87, pp.129. 132, Elsevier Publications

[3] A.M.G. Monteiro et al (2000). Phenol biodegradation by Pseudomonas putida DSM 548 in a batch reactor. Biochemical Engineering Journal 2000, vol-6, pp: 45.53

[4] Warren L. McCabe et al (1993), Unit Operations of Chemical Engineering., Fifth Edition., McGraw-Hill International Publications, Singapore

[5] M. Street et al (1995), Sorption of phenol and p-chlorophenol from water using conventional and novel activated carbons., Water Scientific Research, Vol-29, pp.467

[6] Kyuya Nakagawa, Akio Namba, Shin R. Mukai, Hajime Tamon, Pisit Ariyadejwanich, Wiwut Tanthapanichakoon (2004), *Absorption of phenol and reactive dye from aqueous solution on activated carbons derived from solid wastes.*, Water Research, vol-38, pp. 1791. 1798, Elsevier Publications

[7] A.A.M. Daifullah, B.S. Girgis, H.M.H. Gad (2003), *Utilisation of agro-residues (rice husk) in small waste water treatment plants.*, Materials Letters, Vol-57, pp.1723. 1731, Elsevier Publications

[8] Clessceri, L.S, Greenberg, A.E and Trussel R.R (1989) "standard methods for determination of water and waste water" American public health association Washington, DC, 2005, 5.48-5.53

[9] A.H. Mahvi, A. Maleki and A. Eslami (2004), *Potential for rice husk and rice husk ash for phenol removal in aqueous systems.*, American Journal of Applied Sciences, Vol-1, No.4, pp. 321. 326