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## Removal of Phenol from Aqueous Solutions by Rice Husk Ash and Activated Carbon

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**Abstract:** Experiments have been conducted to examine the liquid-phase adsorption of phenol from aqueous solutions by rice husk ash and granular activated carbon. In this experiment, rice husk ash was prepared at three different temperature: 300, 400 and 500°C. Batch kinetics and isotherm studies were carried out to evaluate the effect of contact time, pH, initial phenol concentration and adsorbent dose. Batch kinetic studies showed that an equilibrium time of 5 h was needed for the adsorption of 10 mg L<sup>-1</sup> phenol concentration. Maximum phenol adsorption capacity of rice husk ashes prepared at 300, 400 and 500°C and granular activated carbon was 0.951, 1, 0.989 and 1 mg phenol g<sup>-1</sup> adsorbent, respectively. Batch studies indicated that the optimum pH for the adsorption of phenol was 5 at 21±2°C. The capacity of phenol adsorption at equilibrium increased with the increase of initial phenol concentration (10-300 mg L<sup>-1</sup>) and decreased with the increase of adsorbents dose (1-10 g L<sup>-1</sup>). Kinetics of adsorption obeyed a first order rate equation. The suitability of the Freundlich and Langmuir adsorption models to the equilibrium data were investigated for each phenol-sorbent system. The results showed that the equilibrium data for rice husk ashes prepared at 400 and 500°C and granular activated carbon could be well by the Freundlich isotherm model, whereas the equilibrium data for rice husk ash prepared at 300°C fitted the Langmuir isotherm model best within the concentration range studied. The studies showed that the rice husk ash could be used as a new and efficient adsorbent material for the removal of phenol from aqueous solutions.

**Key words:** Adsorption, phenol, aqueous solution, rice husk ash, granular activated carbon

### 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 (Lin and Cheng, 2002). Phenolic compounds are common contaminants in wastewater, being generated from petroleum and petrochemical, coal conversion and phenol-producing industries. Phenols are widely used for the commercial production of a wide variety of resins including Phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives and polyamides for various applications (Roostaei and Tezel, 2004; Al-Asheh *et al.*, 2003; Banat *et al.*, 2000; Calace *et al.*, 2002; Qadeer and Rehan, 2002). So, many industries wastes contain Phenolic compounds which are difficult, or impossible to remove by conventional biological treatment processes (Rengaraj *et al.*, 2002a). Phenol is very soluble in water.

That presence in water supplies is noticed as bad taste and odour. In the presence of chlorine in drinking water, phenol forms chlorophenol, which has a medicinal taste, which is quite pronounced and objectionable (Rengaraj *et al.*, 2002a; Aksu and Yener, 2001; Viraraghavan and de Maria Alfaro, 1998). Phenolic compounds 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 (Calace *et al.*, 2002). Stringent US Environmental Protection Agency regulations call for lowering phenol content in the wastewater to less than 1 mg L<sup>-1</sup> (Roostaei and Tezel, 2004; Banat *et al.*, 2000; Qadeer and Rehan, 2002). Also the European Union has classified several phenols as priority contaminants and the 80/779/EC directive lays down a maximum concentration of 0.5 µg L<sup>-1</sup> for total phenols in drinking water (Calace *et al.*, 2002). There are many methods for the removal of phenol from aqueous solutions. These methods have been classified in two principal categories: destructive processes such as destructive oxidation with

ozone, hydrogen peroxide, or manganese oxide and recuperative processes such as adsorption into porous solids, membrane separation, ion exchange and solvent extraction (Roostaei and Tezel, 2004; Banat *et al.*, 2000; Rengaraj *et al.*, 2002a). 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 (Rengaraj *et al.*, 2002b). Activated carbons remove many of the impurities occurring in the water and wastewater. In spite of these characteristics, because of the high cost and variable performance of carbon regeneration, single use materials are desirable (Al-Asheh *et al.*, 2003; Banat *et al.*, 2000; Rengaraj *et al.*, 2002b). This has led many workers to search for more economic, practical and efficient adsorbents (Calace *et al.*, 2002). Among them rice husk is an agricultural waste as by-product of the rice milling industry to be about more than 100 million tones, 96% 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 (Boveri, 2002; Williams and Nugranad, 2000). Since the main components of rice husk are carbon and silica, it has the potential to be used as an adsorbent (Nakbanpote *et al.*, 2000). When rice husk is burn, about 20 wt% of the husk remains as ash. The Rice Husk Ash (RHA) has more than 95 wt% of silica with high porosity and large surface area, because it retains the skeleton of cellular structure (Boveri, 2002; Nakbanpote *et al.*, 2000; Williams and Nugranad, 2000). The aim of this study was to explore the possibility using rice husk ash and to compare the performance and effectiveness of that with granular activated carbon in removing phenol by adsorption from aqueous solutions. The influences of various factors, such as contact time, pH, initial phenol concentration and adsorbent dose on

the sorption capacity were also studied. The Freundlich and Langmuir isotherm models were used to analyze the adsorption equilibrium.

## MATERIALS AND METHODS

**Preparation of adsorbents:** The rice husks used were obtained from the north part of Iran and the Granular Activated Carbon (GAC) used in this study was purchased from Merck Chemicals company. The proximate and ultimate analysis of rice husks are shown in Table 1 (Williams and Nugranad, 2000). For preparation of Rice Husk Ashes (RHA), at first, rice husks were thoroughly washed with distilled water to remove all dirt and were dried at 105°C for 2 h till constant weight. Then, the rice husks were burned at three different temperature: 300, 400 and 500°C (RHA-300, RHA-400 and RHA-500, respectively) for 2 h in a muffle furnace. The rate of heating was 25-35°C min<sup>-1</sup>. Finally, the rice husk ashes were powdered and stored in desiccators until they were used. Physical and chemical properties of the adsorbents are shown in Table 2 (Nakbanpote *et al.*, 2000).

**Phenol solutions:** The test solutions were prepared by distilled of stock phenol solution (1000 mg L<sup>-1</sup>) to the desired concentrations. A stock phenol solution was obtained by dissolving 1 g of phenol, (99.99% from Merck, Germany), in Deionized Distilled Water (DDW) and dilute to 1000 mL. Intermediate phenol solution was obtained by dissolving 10 mL of stock phenol solution in DDW and dilute to 1000 mL and finally, standard phenol solutions containing 1, 2, 2, 3, 4 and 5 mg L<sup>-1</sup> phenol were prepared by dissolving 10, 20, 30, 40 and 50 mL intermediate phenol solution in DDW and dilute 100 mL. Calibration curve was prepared from standard phenol solutions (APHA *et al.*, 1998). The range in initial concentrations of phenol prepared from stock phenol solution varied between 10-300 mg L<sup>-1</sup>.

Table 1: Properties of the rice husks (Williams and Nugranad, 2000)

| Proximate analysis (wt. %) | Ultimate analysis (wt. %) | Component analysis (wt. %) |
|----------------------------|---------------------------|----------------------------|
| Volatiles (59.5)           | Carbon (44.6)             | Cellulose (34.4)           |
| Moisture (7.9)             | Hydrogen (5.6)            | Hemicellulose (29.3)       |
| Ash (17.1)                 | Oxygen (49.3)             | Lignin (19.2)              |
|                            |                           | Ash (17.1)                 |

Table 2: Physical and chemical characteristics of RAH-300, RHA-400, RHA-500 and GAC (Nakbanpote *et al.*, 2000)

| Property                                           | Rice husk ash |          |          | Granular activated carbon |
|----------------------------------------------------|---------------|----------|----------|---------------------------|
|                                                    | 300°C         | 400°C    | 500°C    |                           |
| Color                                              | Black-brown   | Grey     | White    | Black                     |
| Carbon (%)                                         | 38            | 1.88     | 0.2      | 91.6                      |
| Silicon dioxide (%)                                | 32.02         | 79.27    | 81.04    | 0                         |
| pH                                                 | 4.4           | 9.92     | 10.1     | 9.74                      |
| Average pore diameter                              | 4.2           | 14.49    | 15.16    | 3.35                      |
| Total pore volume (mL g <sup>-1</sup> )            | 0.042         | 0.182    | 0.155    | 0.489                     |
| BET Surface area (m <sup>2</sup> g <sup>-1</sup> ) | 20.26         | 50.14    | 40.93    | 583.74                    |
| Particle size (mm)                                 | Powdered      | Powdered | Powdered | <3                        |

**Determination of the phenol in the solutions:** The concentration of residual phenol in the solutions before and after the equilibrium was determined with direct photometric method. At the end, after the preparation of samples according to the standard method, the residual phenol concentrations were measured using spectrophotometer equipment (Spectronic 20D, Milton Roy Company). The absorbance of the colored complex of phenol with 4-aminoantipyrine was read at 500 nm (APHA *et al.*, 1998).

**Kinetic experiments:** Adsorption studies were conducted in a routine manner by the batch technique. Preliminary experiments were performed to determine equilibrium time for each adsorbent. For this purpose, 1 g of each adsorbent was added to 100 mL phenol solution with a known concentration ( $10 \text{ mg L}^{-1}$ ) and initial pH 5 in 100 mL Erlenmeyer flasks. The flasks placed on a rotating shaker (SINA 2000, Iran) with constant shaking at 190 rpm, at  $21 \pm 2^\circ\text{C}$ . The pH of solutions during the contact period (5-480 min) was adjusted at  $5 \pm 0.2$  using small amount of  $0.1 \text{ M H}_2\text{SO}_4$  or  $0.1 \text{ M NaOH}$  as required. All pH measurements were carried out with a pH meter model CG-710. Samples were periodically withdrawn from the shaker and the solutions were separated from the adsorbent by filtration through filter papers (Whatman No. 41 Ashless). After appropriate dilution, the concentrations of phenol in the filtrate were determined with direct photometric method. The effect of pH values (1-13), initial phenol concentration ( $10\text{-}300 \text{ mg L}^{-1}$ ) and adsorbent dose ( $0.1\text{-}1 \text{ g } 100 \text{ mL}^{-1}$ ) on the sorption of phenol by four types of adsorbent was studied.

**Equilibrium experiments:** The equilibrium isotherms were determined at  $21 \pm 2^\circ\text{C}$  under optimized conditions, changing adsorbent dose into the range of  $0.1$  to  $1 \text{ g } 100 \text{ mL}^{-1}$  and using an equilibrium time equal to 300 min. There were two control flasks for each set of Erlenmeyer flasks. One of the control flask contained just the phenol solution with no adsorbent and the other one contained just water and adsorbent with no phenol in the solution. The first control flask was used to check for phenol volatilization and/or adsorption onto walls of the container during the equilibrium period. The second control flask was used to check the existence of organic contamination in adsorbent or in Deionized Distilled Water (DDW). All the experiments were carried out in duplicates and the average value were used for further calculations.

## RESULTS

The adsorption of phenol in aqueous solution on RHA-300, RHA-400, RHA-500 and GAC were examined by optimizing various physicochemical parameters such as contact time, pH, initial phenol concentration and adsorbent dose. Figure 1 shows the effect of contact time on the removal of phenol by RHA-300, RHA-400, RHA-500 and GAC. The adsorption data for the uptake of phenol versus contact time at  $10 \text{ mg L}^{-1}$  initial phenol concentration with  $1 \text{ g}/100 \text{ mL}$  of each adsorbent were carried out in pH value of 5. The results show that phenol removal increases with time and attains equilibrium in 5 h for each adsorbent. Figure 2 represents the effect of initial pH on the removal of phenol by RHA-300, RHA-400, RHA-500 and GAC. Adsorbent dose, initial phenol concentration and equilibrium time were  $1 \text{ g}/100 \text{ mL}$ ,  $10 \text{ mg L}^{-1}$  and 5 hr, respectively. Adsorbents were added separately in the pH range 1-13 and the results are depicted in Fig. 2. It is evident that the removal of phenol

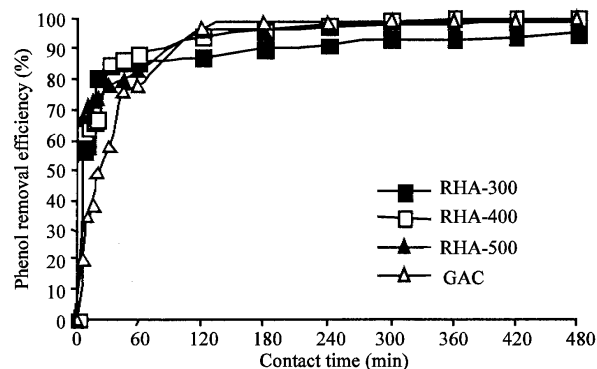


Fig. 1: Effect of contact time on the removal of phenol by RHA-300, RHA-400, RHA-500 and GAC

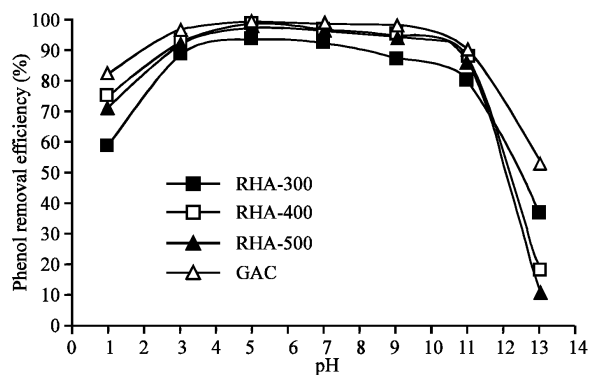


Fig. 2: Effect of pH on the removal of phenol by RHA-300, RHA-400, RHA-500 and GAC

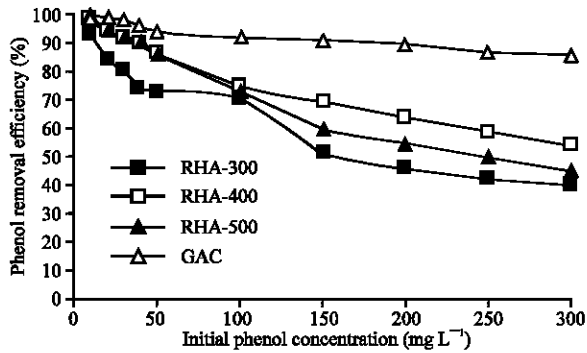


Fig. 3: Effect of initial phenol concentration on the removal of phenol by RHA-300, RHA-400, RHA-500 and GAC

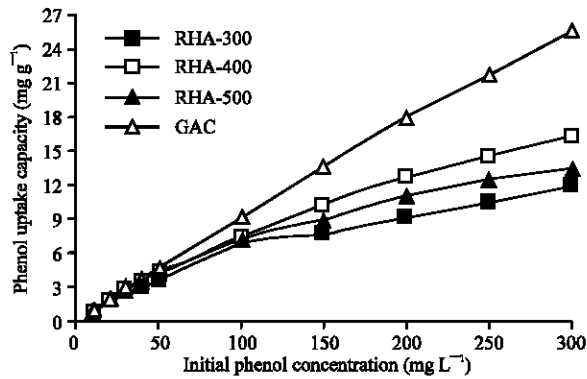


Fig. 4: Effect of initial phenol concentration on the capacity of phenol adsorption by RHA-300, RHA-400, RHA-500 and GAC

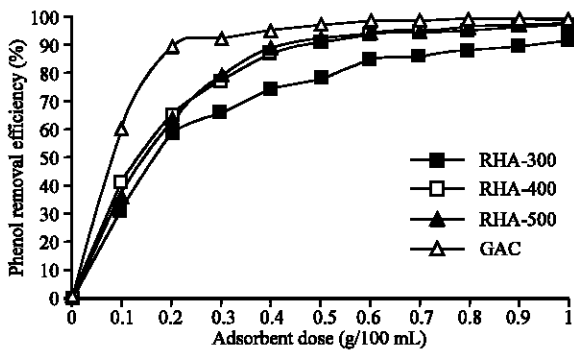


Fig. 5: Effect of adsorbent dose on the removal of phenol by RHA-300, RHA-400, RHA-500 and GAC

by four adsorbents is greatest in the pH of 5 and in the pH values greater than 9 and smaller than 3, the removal efficiency decreases. Figure 3 shows the removal of phenol as a function of initial phenol concentration by

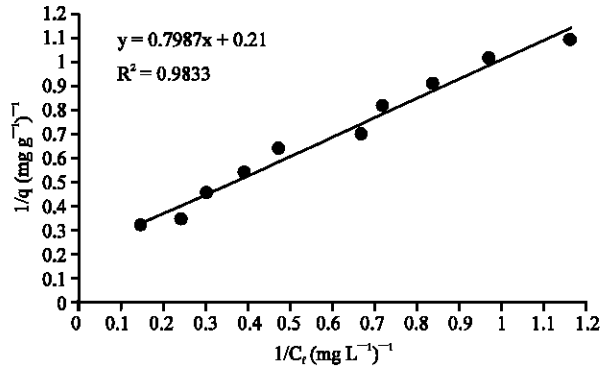


Fig. 6: Langmuir adsorption isotherm for phenol with RHA-300

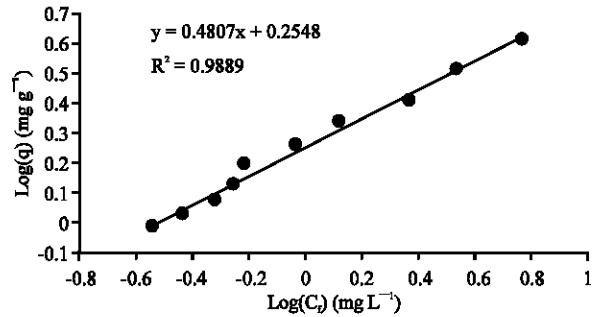


Fig. 7: Freundlich adsorption isotherm for phenol with RHA-400

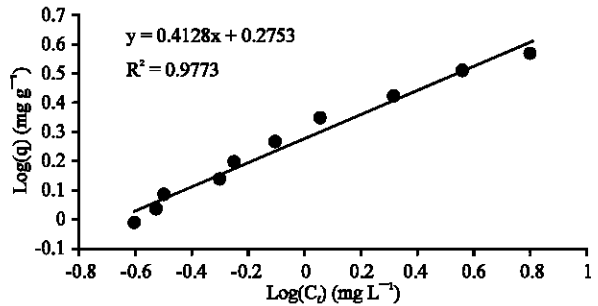


Fig. 8: Freundlich adsorption isotherm for phenol with RHA-500

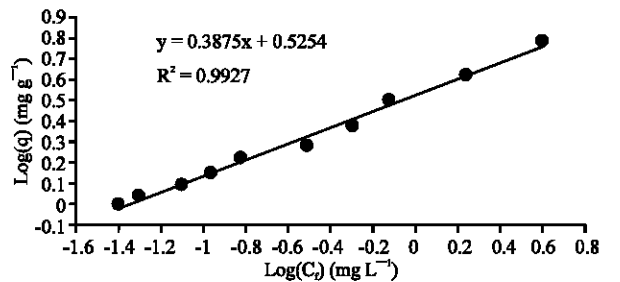


Fig. 9: Freundlich adsorption isotherm for phenol with GAC

Table 3: Parameters of Freundlich and Langmuir isotherm models

| Adsorbent | Freundlich model                                                |        |                | Langmuir model             |                            |                |                |
|-----------|-----------------------------------------------------------------|--------|----------------|----------------------------|----------------------------|----------------|----------------|
|           | K<br>(mg g <sup>-1</sup> ) (L mg <sup>-1</sup> ) <sup>1/n</sup> | 1/n    | R <sup>2</sup> | Q<br>(mg g <sup>-1</sup> ) | b<br>(L mg <sup>-1</sup> ) | R <sub>L</sub> | R <sup>2</sup> |
| RHA-300   | 1.0134                                                          | 0.6371 | 0.9761         | 4.7619                     | 0.2629                     | 0.2756         | 0.9833         |
| RHA-400   | 1.7980                                                          | 0.4807 | 0.9889         | 3.7893                     | 1.0856                     | 0.0843         | 0.9714         |
| RHA-500   | 1.8850                                                          | 0.4128 | 0.9773         | 3.3434                     | 1.6081                     | 0.0585         | 0.9694         |
| GAC       | 3.3527                                                          | 0.3875 | 0.9927         | 3.1279                     | 10.3129                    | 0.0096         | 0.8836         |

RHA-300, RHA-400, RHA-500 and GAC. The capacities of phenol adsorption at equilibrium time by adsorbents obtained from experimental data at different initial concentrations are presented in Fig. 4. Adsorbent dose, equilibrium time and pH were 1 g/100 mL, 5 h and 5, respectively. Figure 5 shows the removal of phenol as a function of adsorbent dose by RHA-300, RHA-400, RHA-500 and GAC. The initial phenol concentration, equilibrium time and pH were 10 mg L<sup>-1</sup>, 5 h and 5, respectively. Adsorbent doses were varied from 0.1 to 1 g/100 mL. The linearized Freundlich and Langmuir adsorption isotherms of each adsorbent for phenol are shown in Fig. 6-9. The Freundlich and Langmuir constants are display in Table 3. The initial phenol concentration, equilibrium time and pH were 10 mg L<sup>-1</sup>, 5 h and 5, respectively.

### DISCUSSION

**Effect of contact time:** The results show that removal of phenol increases with time attains equilibrium in 5 h for RHA-300, RHA-400, RHA-500 and GAC. These results also indicated that the sorption process could be considered very fast because of the largest amount of phenol attached to the sorbent within the first 120 min of adsorption. The phenol removal versus time curves are smooth and continuous leading to saturation, suggesting the possible monolayer coverage of phenol on the surface of the adsorbents (Rengaraj *et al.*, 2002b). The kinetics of phenol adsorption on four adsorbents follow the first order rate equation.

**Effect of pH:** The adsorption of phenol from aqueous solutions is depended on the pH of the solution, which affect the surface charge of the adsorbate species. According to the results, the removal of phenol by four adsorbents is greatest in the pH of 5 and in the pH values greater than 9 and smaller than 3, the removal efficiency decreases. The pH of the aqueous solution of phenol affects its uptake on adsorbent and in general the uptake decreases at lower as well as higher pH values. At lower pH values the uptake of phenol is less due to the presence of H<sup>+</sup> ions suppressing the ionization of phenol and hence its uptake on polar adsorbent is reduced. In the higher pH range phenol forms salts which readily

ionize leaving negative charge on the phenolic group. At the same time the presence OH<sup>-</sup> ions on the adsorbent prevents the uptake of phenolate ions (Rengaraj *et al.*, 2002a).

**Effect of initial phenol concentration:** As seen from the results, the capacity of phenol adsorption at equilibrium time increased with increasing phenol concentration (10-300 mg L<sup>-1</sup>). Increasing the initial phenol concentration would increase the mass transfer driving force and therefore the rate at which phenol molecules pass from the bulk solution to the particle surface. This would results in higher phenol adsorption capacity (Banat *et al.*, 2000). On a relative basis, however, the percentage adsorption of phenol decreases as the initial phenol concentration increases. The equilibrium uptake and adsorption yield were highest for the GAC, which was expected, because of the greater specific surface area and the microporous structure of GAC compared with RHA-300, RHA-400 and RHA-500.

**Effect of adsorbent dose:** According to the results, it is evident that for the quantitative removal of different values of phenol in 100 mL, a high dosage of rice husk ashes is required. The data clearly shows that the GAC is more effective than rice husk ashes for 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.

**Adsorption isotherms:** Several models have been published in the literature to describe experimental data of adsorption isotherms. The Freundlich and Langmuir models are the most frequently employed models. In this work, both models which were used, describe the relationship between the amount of phenol adsorbed and its equilibrium concentration for RHA-300, RHA-400, RHA-500 and GAC. The linear form of the Freundlich isotherm model is given by the relation of

$$\left[ \text{Log } q = \text{Log}(K) + \frac{1}{n} \text{Log}(C_f) \right]$$

The linear form of the Langmuir isotherm model can be represented by the relation of

$$\left[ \frac{1}{q} = \frac{1}{Q} + \frac{1}{bQ} \frac{1}{C_f} \right]$$

The results showed that the equilibrium data for RHA-400, RHA-500 and GAC could be well by the Freundlich isotherm model, whereas the equilibrium data for RHA-300 fitted the Langmuir isotherm model best within the concentration range studied. But, in general,  $R^2$  values, which are a measure of goodness-of-fit, show that both the Langmuir and Freundlich isotherm models could adequately describe the adsorption data. The high value of  $K$ , the Freundlich constant, showed easy uptake of phenol by RHA-400, RHA-500 and GAC. The value of  $K$  is the lowest for the RHA-300. The magnitude of  $Q$  that indicates the amount of phenol per unit weight of sorbent to form complete monolayer on the surface appears to be significantly higher for RHA-300 in comparison to RHA-400, RHA-500 and GAC. The value of equilibrium parameter ( $R_L$ ) also indicates favorable adsorption for RHA-300 (Aksu and Yener, 2001). Similar observation have been reported of the sorption of phenol on; bentonite, organobentonit and palm seed coat activated carbon and the sorption of heavy metals on rice husk (Al-Asheh *et al.*, 2003; Banat *et al.*, 2000; Boveri, 2002; Rengaraj *et al.*, 2002a; Lin and Cheng, 2002; Viraraghavan and de Maria Alfaro, 1998).

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