Potential of Rice Husk and Rice Husk Ash for Phenol Removal in Aqueous Systems

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Abstract: The potential of rice husk and rice husk ash for phenol adsorption from aqueous solution was studied. Batch kinetics and isotherm studies were carried out under varying experimental conditions of contact time, phenol concentration, adsorbent dose and pH. Adsorption equilibrium of rice husk and rice husk ash was reached within 6 hr for phenolic concentration 150-500 µg/L and 3 hr for phenol concentration 500-1300 µg/L, respectively. Kinetics of adsorption obeyed a first-order rate equation. The adsorption of phenol increases with increasing the solution pH value. 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 all the phenol-sorbent systems fitted the Freundlich model best within the concentration range studied. A comparative study showed that rice husk ash is very effective than rice husk for phenol removal. The studies showed that the rice husk ash can be used as an efficient adsorbent material for removal of phenolic from water and wastewater.

Key words: Phenol, Rice Husk, Rice Husk Ash, Adsorption, Aqueous System

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 petrol chemical industries over the past several decades. So, many industrial wastes contain organics which are difficult, or impossible to remove conventional biological treatment processes [1]. In the past several decades, extensive research has been conducted to develop innovative and promising adsorbent material for dealing with the treatment problem of contaminate industrial effluents. The ultimate goal of this endeavor is to identify an effective and expensive adsorbent for the Volatile Organic Compound (VOC) removal from aqueous solution [2]. Phenols as a class of organics are similar in structure the more common herbicides and insecticides in that they are resistant to biodegration. Phenol is very soluble in water. The odor threshold for phenol is 0.04 ppm (U.S.EPA). Their presence in water supplies are noticed as had taste and odor [3]. In the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste, which is quite pronounced and objectionable [4, 5]. 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 [6].

There are many methods such as oxidation, precipitation, ion change, solvent extraction and adsorption for removing phenols and its derivatives from aqueous solution [4, 7].

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 [8, 9]. Activated carbons remove many of the impurities occurring in water and wastewater [9-11]. In spite of these characteristics, because of the high cost and variable performance of carbon regeneration, single use materials are desirable [4, 12]. This has led many workers to search for more economic, practical and efficient techniques. Bottom ash, brick-kilm ash, fly ash, peat, soil, rice husk, wood, saw dust, bagasse and carbonized bark are some new adsorbent used for organic pollutants, [4, 5, 7, 12-14].

In the search for new and low cost agricultural wastes as source material for widely uses. Rice husk are an agricultural waste produced as by-product of the rice milling industry to be about more than 100 million tonnes, 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 [15]. Since, the main components of rice husk are carbon and silica (15-22% SiO_2 in hydrated amorphous form like silica gel), it has the potential to be used as an adsorbent [16, 17]. When rice husk is burnt, about 20 wt% of the husk remains as ash. The rice husk ash has more than 95 wt% of silica with high porosity and large surface area, because it retains the skeleton of cellular structure. These properties of the rice husk ash could be used to synthesize siliceous raw materials such as clay materials [7, 18]. The aim of this study was to explore the possibility using rice husk and rice husk ash for removing phenol from aqueous solution. The influences of various factors, such as initial pH and initial pollutant concentrations on the sorption capacity were also studied. The Freundlich and langmuir models were used to analyze the adsorption equilibrium.

MATERIALS AND METHODS

Preparation of Sorbent*:* The rice husks used were obtained from the north part of Iran. The proximate and ultimate analysis of rice husks are shown in Table 1 [15-17]. The rice husk were crushed and sieved with a 30-mesh siever**.** Then, the husks were thoroughly washed distilled water to remove all dirt and were dried at 100ºC till constant weight. The dried husks were stored in desiccator until used. The rice husk ash obtained from burning of rice husk in electrical oven at 400 ºC for 3 hours. The rice husk ash was sieved with an 80-mesh siever and stored in a desiccator until used. Typical chemical composition of the mineral ash is: 96.34% SiO_2, 2.31% K_2O, 0.45%MgO, 0.41% Al_2O_3, 0.41% CaO and 0.2% Fe_2O_3. Physical and chemical properties of rice husk ash heated at 400 ºC are: 1.88% carbon, 79.27% silicon dioxide. The rice husk ash has a BET surface area of 50.14 m²/g, total pore volume of 0.182 ml/g and average pore diameter of 14.49 nm [17].

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 Merek), in cooled distilled water and dilute to 1000 ml. Intermediate phenol solution was obtained by dissolving 100 ml of stock solution of phenol in distilled water and dilute to 1000 ml and finally, standard phenol solution prepared by dissolving 100 ml intermediate phenol solution in distilled water and dilute to 1000 ml. The range in concentrations of phenol prepared from standard solution varied between 100µg/L to 1300µg/L. 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 pH meter model E520, Metrohm Herisan.

Absorption Studies: 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), and rice husk ash (0.1 to 0.5g) were added to each beaker. The flasks were agitated on a shaker at a100 rpm constant shaking rate for 6hr to ensure equilibrium was reached. For the studies with the rice husk, before analysis, samples were distilled by distillation apparatus according to standard methods [19]. Then, distilled samples analyzed for the remaining phenol. The studies were performed at a constant temperature of 25ºC to be representative of environmentally relevant condition. For the studies with the rice husk ash, before analysis, samples were centrifuged at 5000 rpm for 5 min. and the supernatant fluid analyzed for the remaining phenol. Kinetic experiments were conducted using a know weight of adsorbent dosage and employing phenol concentration. 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.

Analysis of Phenol: The concentration of residual phenol in the sorption medium was determined with direct photometric method. At the end, after the preparation of samples according to the standard methods, the residual phenol concentrations were measured using a spectrophotometer equipment (spectrophotometer DR-2000, HACH). The absorbance of the colored complex of phenol with 4-aminoantipyrine was read at 500 nm [19].

RESULTS AND DISCUSSION

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

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 adsorb ate species. The adsorption of phenol by rice husk and its ash were studied at various pH values [5, 7, 8, 12, 20]. The results are displayed in Fig.1. As was expected, the adsorbed amount decreases with increasing the pH value. This can be attributed to the depending of phenol ionization on the pH value. The ionic fraction of phenolate ion φ_{ions} can be calculated from [6]:

Table 1: Properties of the Rice Husks

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

Table 2: Parameters of Freundlich and Langmuir Isotherm Models

	Freundlich constants			Langmuir constants		
	K	1/n	R^2	Q^0	b	R^2
Rice husk	0.00092	0.195	0.96	0.0022	30.72	0.87
Rice husk ash	0.00092	0.57	0.98	0.886	5.15	0.97

$$\varphi_{ions} = \frac{1}{[1 + 10^{(pk_a - pH)}]}$$

Obviously, φ_{ions} 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 value [6, 16]. 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 [4, 16]. Similar behavior has been reported by [8] for the adsorption of phenol by activated carbon, and adsorption of phenol onto bentonite by [6]. 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 [4, 7].

Effect of Contact Time: The adsorption data for the uptake of phenol versus contact time at 150µg/L initial concentration with 5g rice husk and 700µg/L initial concentration with 0.12gr rice husk ash were carried out in pH value of 7. The results show that equilibrium time required for the adsorption of phenol on rice husk and its ash are almost 6hr and 3hr respectively. 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. This indicates that rice husk ash would require less residence time for the complete removal of phenol compared to rice husk. Fig. 2 shows the effect of contact time on the removal of phenol by rice husk and its ash. The kinetics of phenol adsorption on both rice husk and its ash follows the first-order rate expression.

Effects of Adsorbent Amount: The amount of adsorbent on the efficiency of adsorption was also studied. Figs. 3 and 4 show the removal of phenol by

rice husk and its ash at the solution pH of 7. Adsorbent dosage was varied from 1g to 7g and 0.1g to 0.5g for rice husk and its ash, respectively.

The results show that for removal of 500 µg/l of phenol in 100 ml of solution, a minimum dosage of 0.3gr of rice husk ash is required for 96% removal of phenol. But, with this condition by rice husk, the removal efficiency is 27%. It is evident that for the quantitative removal of different value of phenol in 100 ml a high dosage of rice husk is required. The data clearly shows that the rice husk ash is more effective than rice husk 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 (especially about ash).

Effect of Initial Phenol Concentration: The equilibrium sorption capacities of the sorbents obtained from experimental data at different initial phenol concentration are presented in Fig. 3 and Fig. 4, and Table 2. As seen from results, the sorption capacities of the sorbents increased with increasing phenol concentration while the adsorption yields of phenol showed the opposite trend. When the initial phenol concentration was increase from 150 µg/L to 350µg/L on rice husk and from 500µg/L to 1300µg/L on rice husk ash, the loading capacity increased from 1.56×10^{-6} mg/mg to 1.96×10^{-6} mg/mg of rice husk, and from 2.7×10^{-4} mg/mg to 6.15×10^{-4} mg/mg of rice husk ash. Increasing 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 [20, 21]. On a relative basis, however, the percentage adsorption of phenol decreases (Figs. 2 and 3) as the initial phenol concentration increases. The equilibrium uptake and adsorption yield were highest for the rice husk ash, which was expected, because of the greater specific surface area and the microporous structure of rice husk ash compared with rice husk.

Adsorption Isotherms: Several models have been published in the literature to describe experimental data
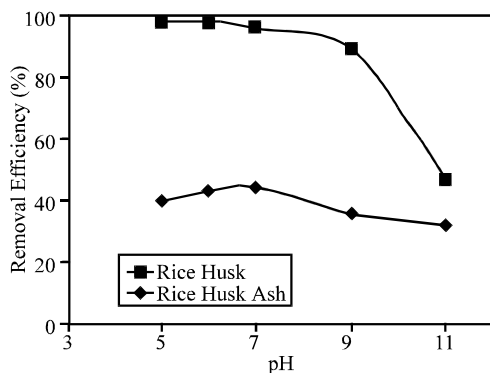
Fig. 1: Effect of pH on the Removal of Phenol by Rice Husk and Rice Husk Ash (Rice Husk Dosage = 3 g/100 ml, Rice Husk Ash Dosage = 0.5 g/ 100 ml, Phenol Concentration = 0.2 mg/L)
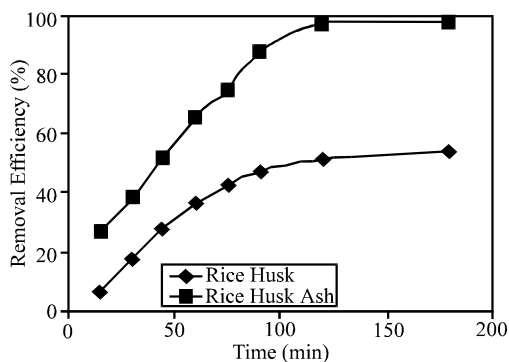

Fig. 2: Effect of Contact Time for the Removal of Phenol by Rice Husk and Rice Husk Ash [(Rice Husk Dosage = 5 g/100 ml, Phenol Conc. = 0.15 mg/L), (Rice Husk Ash Dosage = 0.12 g/100 ml, Phenol Conc. = 0.7 mg/L)]
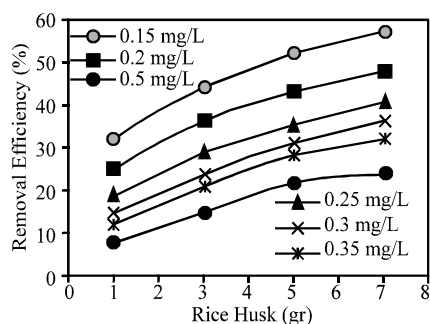

Fig. 3: Effect of Rice Husk on the Removal of Phenol for Various Initial Phenol Concentrations

is of adsorption isotherms. Analysis of the isotherm data is important in order to develop an equation that accurately represents the results and which could be used for design purposes. In this work, both models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration for both rice husk and its ash.
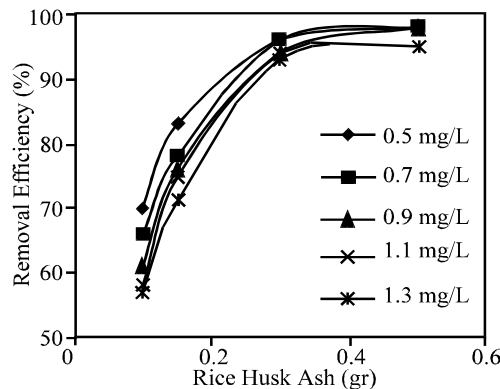

Fig. 4: Effect of Rice Husk Ash on the Removal of Phenol for Various Initial Phenol Concentrations
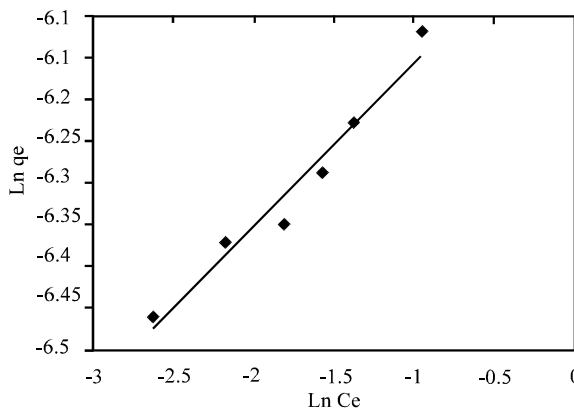

Fig. 5: The Linearized Freundlich Adsorption Isotherm for Phenol with Rice Husk

The linear form of the Freundlich isotherm model is given by the following relation [4, 6, 7, 9, 10, 16]:

$$\ln q_e = \ln K + \frac{1}{n}\ln C_e$$

Where: q_e is the amount adsorbed of equilibrium (mg/mg), C_e is the equilibrium concentration of the adsorbate (mg/L), and K and $\frac{1}{n}$ is the Freundlich constants related to adsorption capacity and adsorption intensity respectively, of the sorbent. The values of K and $\frac{1}{n}$ can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of $\ln q_e$ versus $\ln C_e$ [4, 6, 7, 9, 10, 16]. The linear form of the Langmuir isotherm model can be represented by the following relation [4, 6, 7, 9, 10, 16]:

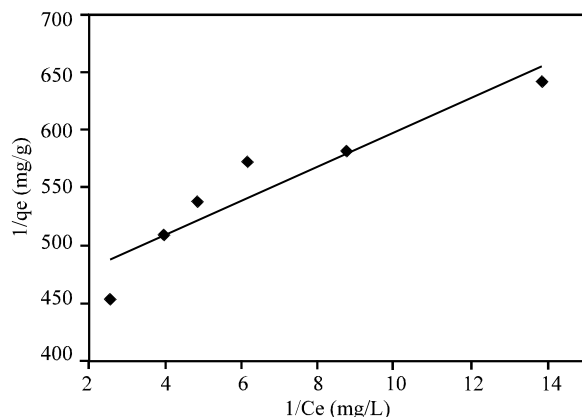$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0}\frac{1}{c_e}$$

[4, 6, 7, 9, 10, 16].
The linearized Freundlich and Langmuir adsorption isotherms of each sorbent for phenol are shown in Fig. 5 to Fig. 8. The Langmuir and Freundlich constants are display in Table 2. The results reveal that the adsorption of phenol on rice husk and its ash obeys the Freundlich adsorption isotherm. But, in general, R^2 Values, which are a measure of goodness-of-fit (Table2), show that both the Langmuir and Freundlich isotherm models can adequately describe the adsorption data. The higher value of k, the Freunlich constant, showed easy uptake of phenol from aqueous solution [4, 7, 8]. The adsorption capacity k is the lowest for the phenol-rice husk system. The n value, which reflects the intensity of sorption, presents the opposite trend, but as seen from table2 for all the sorbents and pollutants, n values were found high enough for separation. The higher fractional value of $\frac{1}{n}$ ($0 < \frac{1}{n} < 1$) Signifies That the surface of the rice husk is heterogeneous in nature [16]. The magnitude of Q^0 indicates that the amount of phenol per unit weight of sorbent to form a complete monolayer on the surface appears to be significantly higher for phenol–rice husk ash system in comparision to rice husk. A large value of b also implies that strong bonding of phenolnoccurred with sorbent [7]. Similar observation have been reported of the sorption of phenol on; bentonite, organobentonite and palm seed coat activated carbon, and the sorption of antimony and cadmium on rice husk [2, 4, 6, 16, 17, 21].

Fig. 6: The Linearized Langmuir Adsorption Isotherm for Phenol with Rice Husk
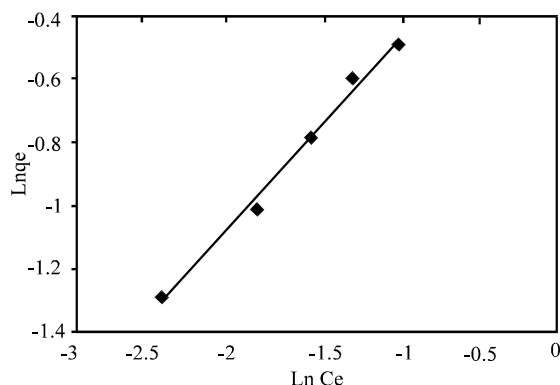
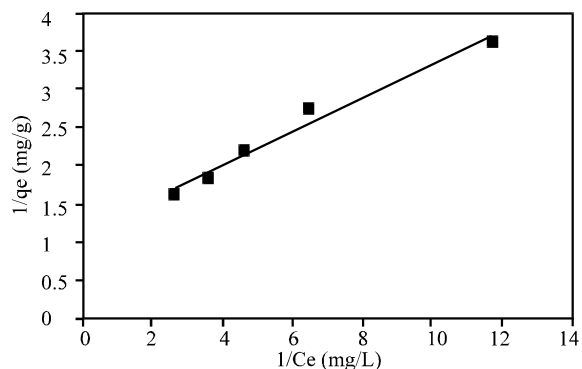Fig. 7: The Linearized Freundlich Adsorption Isotherm for Phenol with Rice Husk Ash

Fig. 8: The Linearized Langmuir Asorption Isotherm for Phenol with Rice Husk Ash

Where: Q^0 (mg/g) and b (L/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and slop of the linear plot experimental data of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$

CONCLUSION

In this study, the ability of rice husk and rice husk ash to bind phenol was investigated as a function of pH and initial phenol concentration. Rice husk and rice husk ash adsorption capacity were strongly dependent on the pH of the solution. The sorption capacity was decreased with an increase in the pH and an increase in the initial phenol concentration. Although rice husk ash had a higher adsorption capacity (0.886 mg/g) for phenol, the experimental results indicate that rice husk's ability to adsorb phenol and, consequently, its possible utilization in the treatment of phenol-contaminated solution, its adsorptive capacity was limited.
Freundlich Langmuir adsorption models expressed the sorption phenomena of phenol to the rice husk and its ash. Consequently, linear regression of the experimental data showed that the Freundlich equation best represented phenol adsorption data. The adsorption of phenol onto both the sorbents follows first-order kinetics. The model parameters would be useful for fabrication and designing of wastewater treatment plants. On the bases of this study, it may be concluded that rice husk and its ash especially, may be used as low-cost, natural and abundant sources for the removal

of phenol. They may also be effective in removing other harmful species such as heavy metal ions present in effluents.

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